STUDIES ON OXIDATIVE DEHYDROGENATION OF n-BUTANE

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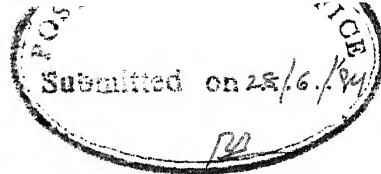
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by

DINESH

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CERTIFICATE

This is to certify that the present work "STUDIES ON OXIDATIVE DEHYDROGENATION OF n-BUTANE" has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

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NOMENCLATURE

a,b,c	:	Lattice parameters, Å
bd	:	1,3 Butadiene
bute	:	Butenes (n-, trans-2 and cis-2)
C	:	Concentration
'd'	:	Interplaner spacing, Å
F	:	Total molar gaseous feed rate, mg mol/min
F_1, F_2	:	Fractions of butane producing butenes and butadiene, respectively
F_3	:	Fraction of butenes producing butadiene
hkl	:	Miller indices used in X-ray diffraction and electron microscopic studies
I/I_o	:	Relative peak intensity used in X-ray diffraction
$K_1, K_2 - - - - K_6$	:	Equilibrium constants
k_1, k_2, k_3	:	Reaction rate constants
p	:	Partial pressure
r	:	Rate of reaction
S	:	Selectivity, mol%
s	:	Standard deviation
t	:	Time
u	:	Conversion of butane to butenes
v	:	Conversion of butane to butadiene
W	:	Total weight of catalyst, g

x	:	Total conversion of butane
Y	:	Yield, mol%

Greek Letters

α, β, γ, ε	:	Different phases of crystal structure
$\triangle H$	:	Heat of reaction, kcal/mol
θ	:	Angle of diffraction, degree
μ	:	micron

Subscripts

A	:	Butane
B	:	Butenes
C	:	Butadiene
O_2	:	Oxygen
o	:	Initial value
t	:	Total number of sites
1	:	Vacant site
O1	:	Oxidised site

SYNOPSIS

Butenes and butadiene are important products of the petroleum industry. A substantial increase in their demand is envisaged in the near future. Traditionally butadiene is produced by dehydrogenation of butenes which in turn may be obtained from n-butane. Butane and butenes are formed as by product of several petroleum refining processes. While butenes have been recovered and utilized for production of butadiene and several other products, butanes are generally used only as a fuel. This is a poor utilization of an important product stream. Conversion of n-butane to more useful products like butenes and butadiene may be of greater economic consideration.

Oxidative dehydrogenation of butenes to butadiene has been commercially practiced. Under certain conditions oxidative dehydrogenation of n-butane to butenes and butadiene may be feasible. Several catalysts have been developed for the abstraction of hydrogen from butenes. However, abstraction of the first hydrogen from a saturated hydrocarbon like n-butane is difficult and hence requires more appropriate catalysts. Abstraction of the first hydrogen atom from the n-butane molecule involves rupture of a strong σ bond between the hydrogen and the carbon atoms under stringent conditions. The hydrocarbon molecule has a tendency to burn off completely rather than dehydrogenate to yield butenes and butadiene under these conditions. Hence,

development of a suitable catalyst is the first important requirement for the dehydrogenation of n-butane to butenes and butadiene.

A review of the literature indicated that bismuth molybdate-iron oxide catalyst on alumina may be a promising catalyst for this purpose [1,2]. Accordingly, catalysts containing bismuth molybdate, iron oxide were developed and their activity and selectivity were studied for the proposed reaction. β-phase bismuth molybdate ($Bi_2O_3.2MoO_3$) and γ-phase bismuth molybdate ($Bi_2O_3.MoO_3$) along with iron oxide were the main constituents of the catalysts.

.The catalysts were characterised in terms of chemical compositions, tap densities, surface areas, thermal stabilities, X-ray diffraction and transmission electron microscopic studies. Effectiveness of these catalysts was studied for the oxidative dehydrogenation of n-butane to butenes and butadiene using a tubular packed bed reactor under the following conditions :

Temperature	:	400-500 °C
Catalyst to feed ratio (W/F)	:	0.6-2.6 $\dfrac{g\ catalyst}{(mg\ mol/min)}$
		(0.5-2 sec contact time)
Oxygen to butane ratio	:	0.5-2.0 mol/mol
Nitrogen to oxygen ratio	:	1.6 (held constant)
Mol bismuth molybdate per 100 mol support	:	0-20
Bismuth molybdate	:	β- and γ- phases.

β-bismuth molybdate was found to be better of the two catalysts used. The reaction was found to be kinetically controlled. At an optimum temperature of 450°C and an oxygen to butane ratio of about 1.5, a per pass yield of 7.25 mol% and a selectivity of 23 mol% with respect to butadiene were obtained. The combined yield of (butenes + butadiene) was 12 mol% and the combined selectivity was 37% under the optimum conditions.

A kinetic model of the reactions based on Hougen-Watson approach (a single site redox mechanism) has been developed.

β-bismuth molybdate-iron oxide catalyst appears to be a promising catalyst for this industrially important reaction. Recommendations for future work have been proposed.

CHAPTER 1

INTRODUCTION

Of recent, there has been a growing concern throughout the world to utilize the scarce petroleum products judicially. Natural gas and associated gas have so far been used mainly as a fuel. They can serve as potential feed stocks in the production of useful petrochemicals like ethylene, propylene, butenes, butadiene, maleic anhydride etc. The Oil and Natural Gas Commission recently reported [3] that about four million tonnes of oil equivalent gas will be available in India during 1983-84. This gas comprises mainly of methane, ethane, propane and butane. In the national interest, the Government has decided that methane-rich gas can be utilized for urea plants. It may also be used to produce methanol, acetylene etc. The stream containing ethane, propane and butane may be used for the production of olefins, diolefins, maleic anhydride and a host of other petrochemicals.

Among the diolefins, butadiene is an important product. As per recent report [4] the world butadiene market is likely to remain tight until about 1990. Butadiene is produced mainly from butenes. It is also obtained as a by-product from hydrocarbon cracking processes. In India, butadiene is produced as a co-product of ethylene from the naphtha cracker at NOCIL, Bombay. It is also produced from a non-petroleum source such as ethanol at the Synthetics Rubber Plant at Bareilly. Butane stream which is normally used as fuel is a potential raw material for butadiene production. The domestic liquid petroleum gas contains large amount of n-butane which may be better utilized for it's conversion

to butadiene.

The present study is aimed at the utilization of n-butane for the production of butadiene. n-Butane may be converted to butadiene through dehydrogenation processes. The conventional dehydrogenation process is endothermic. On the other hand the oxidative dehydrogenation process is exothermic. Higher yields, simplified product separation techniques and lower operating cost are promised by the oxidative dehydrogenation of butenes to butadiene [5]. Hence, oxidative dehydrogenation process appears to be very attractive for conversion of n-butane to butadiene.

Normally, n-butane is first dehydrogenated to butenes and then to butadiene using chromia-alumina catalysts [6,7,8,9] at temperatures of 500-550°C. However, these catalyst tend to loose their activity rapidly due to severe coking problems. With the introduction of a halogen or a halogen-based compounds, particularly iodine and its compounds, the above difficulty could be alleviated and butane could be dehydrogenated to 1,3 butadiene in a single step with good yield and selectivity [8,10,11,12]. However due to severe corrosion problems and prohibitive cost of iodine, this apparently promising process could not be used commercially.

Butane mixed with air can be dehydrogenated to butenes and butadiene over various type of solid catalysts [10,11,13]. This technique appears to be very attractive since the oxygen present in the reaction media prevents the formation of coke on the catalysts. In this way the dehydrogenation of butane to

butadiene may be realised in a single step. This is called an oxidative dehydrogenation process.

Literature on oxidative dehydrogenation of butenes to 1,3 butadiene indicates that bismuth molybdate catalysts are better suited for this process as compared to other catalysts (see Section 2.2). The addition of an iron oxide to bismuth molybdate catalyst has been reported to enhance its activity and selectivity appreciably [1]. The conversion of n-butane to butadiene in a single step was first attempted by Gaspar and Pasternak [14]. Shenoy [15] used the bismuth molybdate-aluminium phosphate catalyst for this process. As observed for dehydrogenation of butenes to butadiene it appears that the activity of bismuth molybdate catalyst may be improved with the addition of iron oxide for the single step conversion of n-butane to butadiene also.

It follows from the above discussion that bismuth molybdate-iron oxide-alumina may be a suitable catalyst for direct conversion of n-butane to butadiene. Accordingly, the present work was undertaken to develop suitable catalysts for this industrially important reaction. The catalysts were characterised and their effectiveness for the oxidative dehydrogenation of n-butane to 1,3 butadiene has been studied using a packed bed tubular reactor. The effect of process variables like space velocity, catalyst concentration, temperature and oxygen to butane ratio on the conversion of n-butane and on the yield and selectivity of butadiene as well as of combined (butenes + butadiene) has been examined. A kinetic

model based on Hougen-Watson approach has been also developed for the oxidative dehydrogenation of n-butane to 1,3 butadiene.

CHAPTER 2

LITERATURE SURVEY AND SELECTION

OF A CATALYST

The dehydrogenation of butane to butenes and butadiene is
an industrially important reaction. Several processes based on
different raw materials to produce olefins and diolefins have
been described in literature. In the following sections the
literature on the production of butenes and butadiene are revie-
wed briefly.

2.1 Thermodynamic Aspects

The main reaction sequence for the conventional dehydro-
genation of butane may be represented by the following scheme :

$$C_4H_{10} \longrightarrow C_4H_8 \; + \; H_2 \; ; \; \Delta H = +28.5 \text{ k cal/mol} \qquad (2.1)$$
Butane   Butene

$$C_4H_8 \longrightarrow C_4H_6 \; + \; H_2 \; ; \; \Delta H = +28 \text{ k cal/mol} \qquad (2.2)$$
Butene   Butadiene
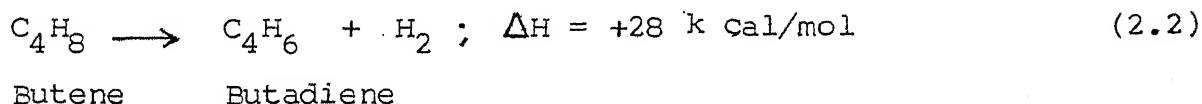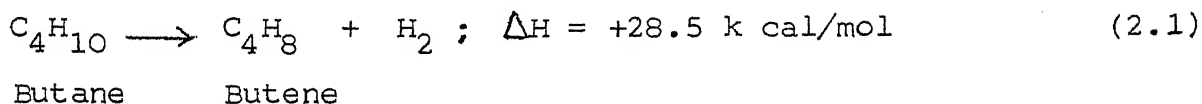
The reactions (2.1) and (2.2) are highly endothermic. Begly [16]
studied the equilibrium conditions for the dehydrogenation of
butane and found that the maximum equilibrium yield of butenes
occurs at a pressure of 0.1 atm. and a temperature of 540°C. The
maximum equilibrium yield of butadiene from butenes is about 90%
and occurs at 125 mm Hg pressure at 790°C.

At high temperatures, considerable thermal and catalytic
cracking occurs. Consequently, the temperature to be used in a

commercial plant has to be substantially below 600°C. At lower temperatures, the per pass yields are poor. Further, under practical conditions of low pressure operation, the yields are considerably lower than the equilibrium yields. Hence suitable catalysts have to be developed which may permit the use of lower temperatures. Steam may be used as a diluent to realise the benefits of low pressure conditions.

2.2 Dehydrogenation Processes

The commercial processes for the production of butenes and butadiene may be classified as :

1. Thermal dehydrogenation process
2. Catalytic dehydrogenation process

The thermal cracking of naphtha for the production of ethylene and propylene results in the formation of butenes and butadiene as co-products in appreciable amounts [8]. However, this process has the disadvantage due to undesirable side reactions. Russel, et al. [17] obtained only 40% of the theoretical yield of butadiene from butenes at 600°C and 100 mm Hg pressure. Therefore, thermal dehydrogenation process is commercially unattractive.

The catalytic dehydrogenation processes may be classified as under :

(i) Houdry process

(ii) Steam dilution process

(iii) Oxidative dehydrogenation process

Houdry process was the first commercial process used for the conversion of mixed streams of n-butane and butenes to butadiene [8]. It employed a catalyst consisting of 15-20% chromia on activated alumina. A conversion of about 63% butane to butadiene was reported [18].

The steam dilution process is generally used for the dehydrogenation of butenes to butadiene. In this process steam is used as a diluent which has the effect of lower pressure. The presence of steam also acts as a source of heat supply, controls the side reactions and prevents the coke deposition on the catalyst. Considerable efforts have been made for the development of suitable catalysts for this process [8].

The dehydrogenation of n-butane or butenes to butadiene yields hydrogen as one of the reaction products. Build up of hydrogen concentration in the product stream imposes a thermodynamic limitation on the equilibrium conversion. If, however, this hydrogen is utilized, say by some simultaneous oxidation process, the equilibrium can be shifted to the favourable direction. In addition, this oxidation reaction will generate sufficient heat to counterbalance the endothermic dehydrogenation reaction. This oxidative dehydrogenation process is of great practical significance. Calvin et al. [19] have found the oxidative dehydrogenation process to be far better than the conventional dehydrogenation process.

The oxidative dehydrogenation may be achieved in the

following two ways :

    (a) Halogenative dehydrogenation process,

    (b) Oxidative dehydrogenation process.

In the halogenative dehydrogenation process use is made of a halogen which combines with the hydrogen. Experimentally the gaseous mixture, containing hydrocarbon, air and halogen may be passed over a catalyst. The halogen may be regenerated from the resultant hydrogen halide by its reaction with oxygen in a separate stage [20]. The following main reactions with iodine illustrate the general process scheme

$$C_4H_{10} + I_2 \rightleftharpoons C_4H_8 + 2HI \qquad (2.3)$$

$$C_4H_8 + I_2 \rightleftharpoons C_4H_6 + 2HI \qquad (2.4)$$

$$4HI + O_2 \rightleftharpoons 2I_2 + 2H_2O \qquad (2.5)$$
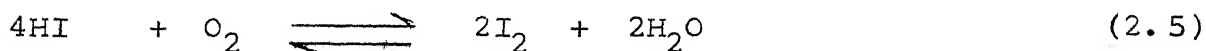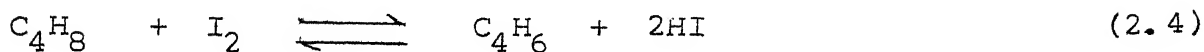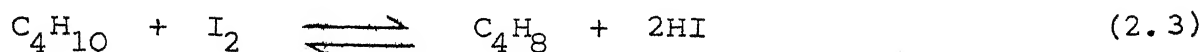
The halogenative oxidation process, although attractive theoretically, could not gain commercial success due to high corrosive conditions and prohibitive cost of iodine.

The oxidative dehydrogenation process uses a mixture of hydrocarbon and oxygen (usually air) to which steam may be added. The mixed stream is passed over a suitable catalyst. The catalysts recommended for the oxidative dehydrogenation of n-butenes are generally mixtures of oxides or phosphates of metals from Groups V (Bi, Sb, As, P, V) and VI (Cr, Mo, W) of the periodic table

[5,11,21-30]. The catalysts consisting of pure metal oxides alone are not found to be very selective and give poor conversions. However, a combination of oxides of metals from neighboring groups are found to enhance the conversion as well as the selectivity to a greater extent. The combinations based on Bi-Mo and Sb-Sn are probably the most prominent catalysts. The oxidation of butenes over a bismuth molybdate catalyst has been studied by different workers [11,21,27,31-38]. Adams et al. [31,32] and Bleijenberg et al. [33] have reported selectivities of 90-95% at conversions ranging from 20-80% for the conversion of n-butene to butadiene at 460°C. Skarchenko [11] observed that the yields of the diolefins during the oxidative dehydrogenation of the individual butylene isomers increase in the order : 2-trans-butene, 2-cis-butene, 1-butene. Similar observations have been reported by Adams et al. [32] and Keizer et al. [34].

Many catalysts containing antimony oxide are found effective for the dehydrogenation of butenes to butadiene. Bakshi et al. [39] found that the catalysts containing oxides of antimony and iron were very selective for this reaction. Boreskov and co-workers [40-42] also studied the antimony oxide systems containing iron and found that this catalyst gave a good selectivity for butadiene. However, catalysts with antimony and tin were found to be less effective than those based on bismuth molybdates. The addition of iron oxide to bismuth molybdate catalyst was found to enhance its catalytic activity significantly [1,30,43].

Recently a considerable Patented literature has appeared
on the direct oxidative dehydrogenation of n-butane to butadiene.
The development of a suitable catalyst appears to be the main
objective of these studies [14,15,29,44-60]. Table 2.1 summarises
the broad observations made by different workers on the oxidative
dehydrogenation of n-Butane. Some Patented literature on the
oxidative dehydrogenation of n-butane describe the reactor type.
Mc Donald et al. [61] used a fluidised bed reactor while Lester
[62] designed a reactor in which air and butane streams were
separated by a porous concentric tube containing an oxygen transfer
agent. The hydrogen generated during the dehydrogenation of butane
diffuses across the porous wall into the air stream, thus reducing
the hydrogen partial pressure and increasing the yield of butenes
and butadiene. Kovaleva and Tulupov [63] have studied the oxidative
dehydrogenation of n-butane at low temperatures (170-200°C) using
a complex catalyst.

2.3   Choice of a Catalyst

The dehydrogenation of butane involves the abstraction of
the hydrogen atoms from the parent molecule. The paraffinic
hydrocarbons act upon the metal oxide catalysts more or less as
electron donating agents; this tendency being very weak in butane,
its dehydrogenation activity will be governed by the activity of
the surface sites. Therefore, an efficient catalyst will be the
one which has either active Lewis acid sites that can abstract

TABLE 2.1   OXIDATIVE DEHYDROGENATION OF n-BUTANE

Feed	Catalyst	Temperature	Conversion,%	Selectivity,%		Yield,%		Reference
				Butadiene	Butenes	Butadiene	Butenes	
$1C_4H_{10}, 1.4O_2, 40H_2O$	Oxides of (Sb 15,V 7.0, Ni 4.0,Th 0.5,Ti 0.1%) + Al_2O_3	600–620°C	28.4	50	–	–	–	44
$1C_4H_{10}, 2O_2$	Mo–Bi–Co–Ni–Fe–Cr	450–500°C	–	–	50	–	–	45
C_4H_{10}, C_4H_8, O_2	CoO–MoO_3	450–600°C	–	–	–	–	–	29
C_4H_{10},Air,H_2O	1Ni,1 Mg, 0.11 P	1100°F	–	25.5	–	–	–	46
C_4H_{10},Air,H_2O	Ni 59.3,Mg 5,S 16.5%	1000°F	29.8	–	–	5.7	–	47
$C_4H_{10}, 1.5O_2, 2OH_2O$	1 Mo,31.4 Mg,3% V_2O_5	570°C	–	–	–	36.6	–	48
C_4H_{10}, O_2	Ni SC_4	–	29	3.6	11.1	3.6	–	49
C_4H_{10}, O_2, N_2	Ba Fe_2O_3,PbO,ZnO,Al_2O_3	580°C	73	–	–	24	34	50
$C_4H_{10}, 22.9H_2O$	Ni, P oxide	1000°F	42.3	–	–	12.7	10.8	51
C_4H_{10}, O_2, H_2O	TiO_2, WO_3, Al_2O_3	1050°F	35.1	38.6(butadiene +butenes)	–	–	–	52

TABLE 2.1 Continued

Feed	Catalyst	Temperature	Conversion,%	Selectivity,% Butadiene	Selectivity,% Butenes	Yield,% Butadiene	Yield,% Butenes	Reference
C_4H_{10}, Air	V_2O_5, K_2SO_4, SO_3	450–650°C	—	—	—	—	—	53
C_4H_{10}, Air, H_2O	Ni PO_4	1200°F	43.4	67.2 (butadiene +butene)	—	—	—	54
C_4H_{10}, 1.4O_2, 40H_2O	oxides of (Sb 15, V 7, Ni 4, Th 0.5%)+Al_2O_3	550–650°C	28.4	60 (butadiene ÷butenes)	—	—	—	55
C_4H_{10}, 0.9O_2, 26H_2O	Sb_2O_3 7–12% NiO 5–10%, V_2O_5 2.5%, γ-Al_2O_3	—	—	—	—	—	—	56
C_4H_{10}, 10 Air	MoO_3 22%, MgO 4.1%, TiO 3.9%	590°C	48.2	75.1	—	36.2	—	57
C_4H_{10}, 1.5Air, 20H_2O		—	—	—	—	—	—	58
C_4H_{10}, Air	MoO_3, MgO, TiO_2	590°C	—	—	—	—	—	59
C_4H_{10}, 10O_2	MoO_3, $AlPO_4$	—	40	67	—	—	—	14
C_4H_{10}, O_2, N_2	Bi_2O_3 2MoO_3, $AlPO_4$	400–500°C	26	9.4	—	—	—	15

hydrogen atoms from butane as hydride ions, or has suitable Bronsted basic sites which can abstract protons from a butane molecule or both. Acidic sites consisting of metal cations are then necessary for absorbing the remainder of the butane molecule. Thus the dehydrogenation of butane can proceed by the step wise abstraction of hydrogen over these active sites.

Gaspar and Pasternak [14] used molybdenum oxide on aluminium phosphate for the dehydrogenation of butane in the presence of oxygen. Mo^{6+} ions provide good active centres for the adsorption of olefins. However, the oxygen, O^{2-} ions associated with the molybdenum tetrahedra are not mobile, and hence are not efficient in oxidising the hydrogen abstracted from the butane molecule. Lattice oxide, O^{2-} associated with Bi^{3+} has been proven to be very mobile, and can oxidise the abstracted hydrogen easily.

Shenoy [15] used bismuth molybdate-aluminium phosphate catalyst for the one-step oxidative dehydrogenation of n-butane. It has been noted [1,30,43] that the activity and the selectivity of the Fe-Bi-Mo oxide catalyst in the oxidative dehydrogenation of butenes to butadiene were higher than those of the bismuth molybdate catalyst. Considering this fact, it was proposed to incorporate iron oxide into bismuth molybdate catalyst and use it in the present study.

Among different phases of bismuth molybdate, $Bi_2O_3 \cdot MoO_3$ (Koechilinite or γ-phase) and $Bi_2O_3 \cdot 2MoO_3$ (Erman or β-phase) were chosen for the present study. Shenoy [15] found that the

$Bi_2O_3 \cdot 3MoO_3$ was not a good dehydrogenation catalyst. Alumina contains more loose oxygen than aluminium phosphate and oxygen is highly desirable for this process. Alumina should, therefore, be preferred over aluminium phosphate as a carrier. Hence, the bismuth molybdate (in beta and gamma phases both) containing an iron oxide and supported on alumina is used as a catalyst in the present study.

CHAPTER 3

MATERIALS, CATALYST PREPARATION AND EXPERIMENTAL PROCEDURE

3.1   MATERIALS

Gases

n-butane, oxygen and nitrogen were used in this study. C.P. grade n-butane was obtained from M/s Matheson Gas Company, East Rutherford, N.J., U.S.A. Its purity was reported to be 99 mol% minimum, containing small amount of isobutane and 2-2-dimethyl propane.   Technical grade oxygen and nitrogen were obtained from M/s. Indian Oxygen Ltd., Kanpur, India.   The gases had a minimum purity of 99.5 mol%.

Compressed air was used during the heating and cooling of the reactor furnace.   It was also used to flush the gases from the reactor at the end of experiments.   Air was passed over a bed of calcium chloride and activated charcoal to remove moisture, carbon dioxide and other impurities.

Chemicals

A variety of chemicals and reagents were used for the preparation of catalysts and analysis of products.   A.R.   grade bismuth nitrate of 98.97% purity was used in the catalyst preparation.   Bismuthyl nitrate was prepared in the laboratory as generally per procedure described by Mellor, J.W. [64].   500 g of bismuth nitrate were placed in a 4 l beaker to which 2.5 l of distilled water were added and the contents were stirred vigorously for about 5 minutes.   The bismuthyl nitrate slurry, thus obtained, was filtered, washed with water and the cake was dried at 80°C

for 24 hours in an oven.

High purity grade molybdic acid, obtained from M/s.
Reachim, U.S.S.R., was used in this study. It was found to
contain 86.94% MoO_3 by weight [15]. Ammonium-para-molybdate
reported to contain 82.5% MoO_3 by weight was used. G.R. grade
ammonia solution containing 25 wt% ammonia was obtained from
Sarabhai Chemicals, Baroda, India. A.R. grade, nitric acid was
used.

3.2 Catalyst Preparation

The bismuth molybdate catalysts were prepared by the
procedures suggested by Batist and co-workers [65,66].

γ -Bismuth molybdate ($Bi_2O_3 \cdot MoO_3$) was prepared in the labo-
ratory by the procedure suggested by Konings et al. [66]. 114.940
(0.4 mol) of bismuthyl nitrate were added to 34.686 g (0.2 mol)
of molybdic acid, suspended in 2 l of boiling water in an agitated
reactor. A white slurry first formed, which turned to lemon yellow
after about three hours stirring. The suspension was stirred
vigorously for about 20 hours under boiling conditions. The mass
was then cooled and filtered. The washed cake was dried at 110°C
for about 24 hours in an oven. The filtrate was analysed for
bismuth content by atomic spectra. Only traces of elemental
bismuth were observed. The dry bismuth molybdate as obtained by
the above procedure was ground to a fine powder. It was then
calcined in a muffle furnace at 500 $\pm$ 10°C for 10 hours. The

chemical composition of the compound was determined by the atomic spectra method (see Appendix I).

β-Bismuth molybdate ($Bi_2O_3 \cdot 2MoO_3$) was prepared by the method suggested by Batist et al. [65]. For 0.5 mol of β-bismuth molybdate batch, 490.075 g (1 mol) of bismuth nitrate were dissolved in 180 cm^3 of nitric acid and 2 l of water in a beaker. 174.490 g of ammonium-para-molybdate were dissolved in 2 l of water and 50 cm^3 of ammonia solution (0.91 sp. gr.) in another beaker. The ammonium molybdate solution, prepared as above, was then added to the bismuth nitrate solution resulting in a white precipitate of β-bismuth molybdate. The pH of the slurry was raised to about 6.5 by addition of dilute ammonia solution to complete this pre-cipitation. It was filtered and the washed cake was dried at 110°C for about 24 hours to obtain a faint yellow colored product. The powdered material was then calcined at 500 $\pm$ 10°C for about 10 hours. The composition of the compound was determined by the atomic spectra method (see Appendix I).

Catalyst Support

An alumina containing known amount of iron oxide, and small amounts of magnesium and chromium oxide was used as a support for the bismuth molybdate catalysts. This support was obtained from M/s. Associated Cement Company Ltd., Bombay, India. This material was used as a catalyst by Katiyar and Gehlawat [2] for the oxidative dehydrogenation of butylenes to butadiene.

This catalyst support has been denoted as I(K) in this study.

Bismuth Molybdates-I(K) Catalysts

Catalysts containing different amounts of bismuth moly-bdates (β-and γ-phases) and I(K) were prepared under identical conditions. In a typical instance 100 g of finely powdered I(K) catalyst were heated at 600 $\pm$ 10°C for 3 hours in a muffle furnace. After cooling, 35.0 g of $Bi_2O_3.2MoO_3$ were mixed with this I(K) support. Acetone was added to completely submerge this mixture. This catalyst slurry in acetone was homogenised in an air tight homogeniser for about two hours. The acetone was then allowed to evaporate at room temperature and the mixture was dried in an oven at about 110°C. The dry catalyst was pelle-tized in an 'APEX' hand operated hydraulic press machine. 0.6 mm dia.and about 1 cm long pellets were obtained by applying a pressure of 4 to 5 ton on 65.09 mm dia.ram. These pellets were broken and 3-5 mm size fraction was selected. It was activated at 500 $\pm$ 10°C for about 10 hours in a muffle furnace. The catalyst was cooled and stored in a desiccator for use.

3.3 Experimental Set-up

A schematic diagram of the experimental set-up is shown in figure 3.1. The set-up was essentially the same as that used by Shenoy [15]. The gas flow rates were controlled by fine needle valves and were measured by capillary flow meters. An air inlet was also provided and air flow rate was measured by

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Fig.3.1 – Experimental setup.

1. Butane cylinder
2. Nitrogen cylinder
3. Oxygen cylinder
4. Air compressor
5. Capillary flow meter
6. Rotameter
7. $CaCl_2$ drying tubes
8. Reactor tube
9. Furnace
10. Catalyst bed
11. Inert packing
12. Cooler condenser
13. Separator
14. Temperature measuring device
15. Three-way stop-cock
16. Gas sampler

TC1, TC2–Thermocouple
V_1, V_2, V_3–Needle valves

Sample for Orsat analysis

Vent

Sample to gas chromatograph

Thermo-meter

TC1

TC2

Top cap

Bottom cap

Sample to gas chromatograph

Air

O_2, N_2

n-C_4H_{10}

a rotameter. The flow meters were calibrated using a wet gas meter and a soap bubble meter. Drying tubes containing calcium chloride were provided in the gas flow loops to eliminate the moisture.

A tubular fixed bed reactor consisted of a 304-type stainless steel tube of 1.51 cm ID and 62.5 cm long. The lower part of the reactor was loaded with 12.8 g catalyst. It occupied a volume of about 15 cm^3. The catalyst was sandwiched between two porcelain packings. Two 200 mesh wire screens were placed at the ends of the catalyst bed to prevent the loss of small catalyst particles during operation. Two chromel-alumel thermocouples protected by 6 mm OD stainless steel sheaths were used to measure the temperature at the entrance and exit of the catalyst bed.

The reactor assembly was placed in a 4.2 cm ID vertical tubular furnace. The catalyst bed was adjusted to be in the centre of the furnace. An 'ALNOR N-15'-Type temperature controller of 0-880°C range was used to control the reactor temperature. The effluents from the reactor were cooled by a water jacketed cooler-condenser. Condensate from the product stream was collected in a graduated pipette trap. The temperature of the effluent gases from the cooler condenser was measured by a thermometer. A three-way stop cock installed in the exit gaseous stream enabled samples for chromatographic analysis or for Orsat analysis or for venting off gases.

3.4 Experimental Procedure

The furnace was switched on and air was passed through the reactor at a flow rate of about 200 cm^3/min. When the desired temperature was attained, the air flow to the reactor was stopped and simultaneously preset flow rates of nitrogen and oxygen were introduced. After reaching steady state conditions, butane supply was introduced into the reactor. After about 10 minutes, when the temperature of the reactor bed was stabilised the combined inlet gas flow rate was measured using a soap bubble flow meter. The sample of inlet gas mixture was collected in a gas sampler. A gas-tight syringe was used to inject 5 ml gas sample into the gas chromatograph for analysis of inlet gas mixture. Similar samples for reactor effluent gases were collected for chromatographic or Orsat analysis. The amount of condensate formed was measured using a graduated pipette trap over a period of time.

3.5 Analytical Methods

A model AC gas chromatograph supplied by the Chromatography and Instruments Company, Baroda, India, was used for gas analysis. The unit was equipped with a thermal conductivity detector model AC-1-TC. The detector output signals were recorded using an Omega recorder of 1 mV range. High purity nitrogen was used as a carrier gas.

A 6 mm dia. and 7.75 m long DMS column was used for the gas analysis. It was obtained from M/s. Synthetics and Chemicals

Limited, Bareilly, India. Table 3.1 gives full specifications of the DMS column.

TABLE 3.1   SPECIFICATIONS OF THE DMS COLUMN

Column material	DMS-E (Dimethyl-sulpholane)
Support material	C-C-222
Length of the column	7.75 m
Particle size	60-80 mesh
Packing density	0.62317 g/cm^3

The chromatographic analysis of the products was carried out at a column temperature of 35°C and carrier gas flow rate of 40 cm^3/min.

A typical chromatogram is shown in Fig. 3.2.

DMS column resolved a pure hydrocarbon gas mixture such as methane, ethane, ethylene, propane, propylene, n-butane, n-butene, trans-2-butene, cis-2-butene and 1,3 butadiene completely. However, in the presence of oxygen, carbon monoxide and carbon dioxide, the picture was somewhat different. For example, carbon dioxide and propane emerged as a single peak. Similarily, there was considerable overlapping for the peaks of methane, carbon monoxide and oxygen. This necessitated the use of Orsat analysis for an independent determination of carbon dioxide, oxygen and carbon monoxide. Table 3.2 gives the absorbents used for Orsat analysis.
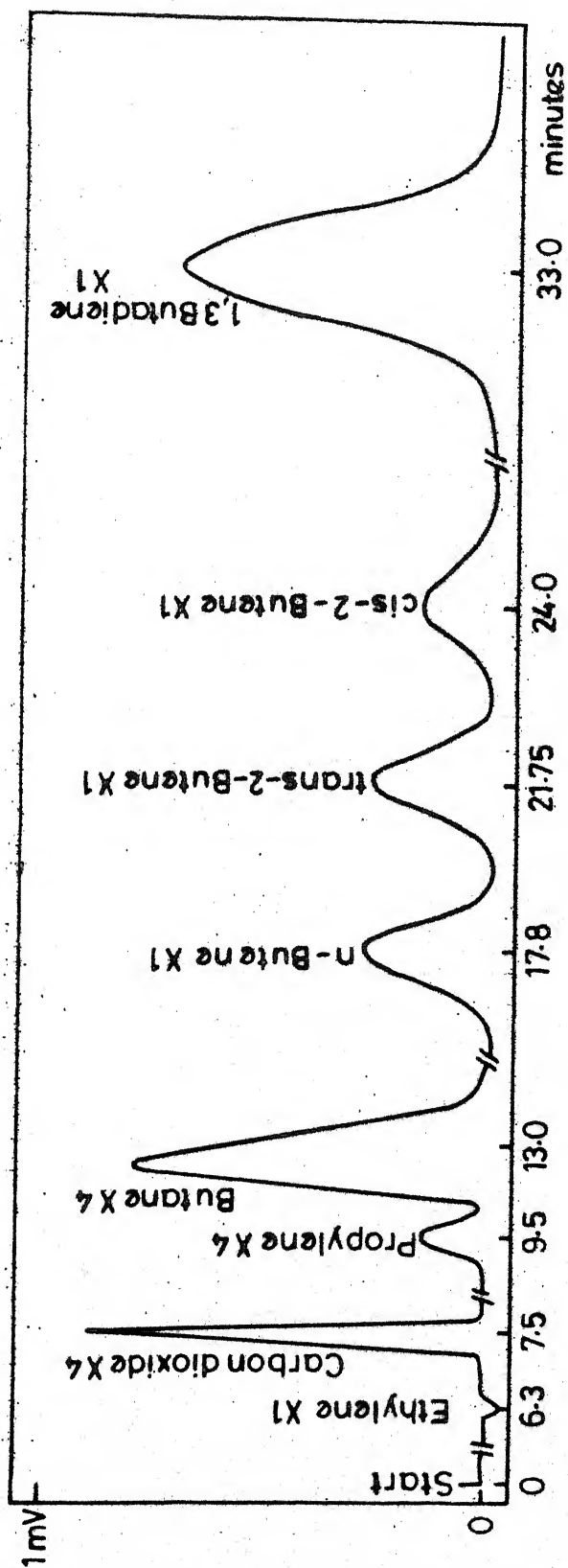
Fig.3.2 – Sample chromatogram.

Column : DMS (Dimethyl – sulpholane), 6mm dia, 7.75m long

Carrier gas: Nitrogen, 40 cc/min

Temperature : 35°C

Detector : Thermal conductivity

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TABLE 3.2 ABSORBENTS FOR ORSAT ANALYSIS

Gases	Absorbent
Carbon dioxide	Potassium hydroxide
Oxygen	Sodium dithionite
Carbon monoxide	Acidic cuprous chloride

3.6 Calibration of Chromatograph

Known amounts of pure gas samples (obtained from Matheson
Gas Company, East Rutherford, N.J., U.S.A.) were injected into
the column using a Hamilton gas-tight microliter syringe for
calibration of the chromatograph. The retention time of the
different hydrocarbon gases at specified conditions are given
in Table 3.3.

TABLE 3.3 RETENTION TIME FOR VARIOUS HYDROCARBON GASES

Column	:	DMS	Carrier gas flow rate	:	40 cc/min
Temperature	:	35°C	Carrier gas	:	Nitrogen

Species	Retention time, min
Methane	4.5
Ethane	5.5
Ethylene	6.3
Propane	7.5
Propylene	9.5
n-Butane	13.0
n-Butene	17.8
trans-2-Butene	21.75
cis-2-Butene	24.0
1,3 Butadiene	33.0

3.7 Definitions

Terms such as conversion selectivity and yield have to be defined properly. Following definitions were used in this study:

$$\text{Conversion, mol\%} = \frac{\text{mols of butane converted}}{\text{mols of butane fed}} \times 100$$

Selectivity,

(a)   w.r.t. (butenes + butadiene), mol%

$$= \frac{\text{mols of net (butenes+butadiene) formed}}{\text{mols of butane converted}} \times 100$$

(b)   w.r.t. butadiene

$$= \frac{\text{mols of net butadiene formed}}{\text{mols of butane converted}} \times 100$$

Yield,

(a)   w.r.t. (butenes+butadiene), mol%

$$= \frac{\text{mols of net (butenes+butadiene) formed}}{\text{mols of butane fed}} \times 100$$

(b)   w.r.t. butadiene, mol%

$$= \frac{\text{mols of net butadiene formed}}{\text{mols of butane fed}} \times 100$$

Model calculations for these quantities have been given in Appendix II.

CHAPTER 4

CHARACTERISATION OF BISMUTH MOLYBDATE IRON(K) CATALYST

The activity of a catalyst depends upon its solid state properties like crystal structure, specific surface area and thermal stability. These properties, therefore, are helpful in understanding the catalytic behaviour of materials. Accordingly, the catalysts used in the present study were characterised in terms of their chemical composition, tap density, specific surface area, thermal stability, microstructure and crystal structure. As Fe_2O_3 is one of the important ingredient of the support, the magnetic behaviour was also examined.

4.1 Chemical Composition

Bismuth molybdates were prepared in two stoichiometric compositions by varying bismuth to molybdenum ratio . The 1:1 bismuth molybdate ($Bi_2O_3.2MoO_3$) existing in β -phase was prepared by the precipitation method [65] . The γ -phase (2:1) bismuth molybdate ($Bi_2O_3.MoO_3$) was prepared by the slurry reaction method [65,66]. The molybdenum and bismuth contents of the catalysts thus obtained were determined using Atomic Absorption Spectroscopy technique, as per detail given in Appendix I. This study confirmed the presence of Bi and Mo in desired stoichiometric ratios.

A catalyst consisting of Al_2O_3, Fe_2O_3, MgO and Cr_2O_3 as per composition given in Table 4.1 was obtained from M/s. Associated Cement Companies Ltd., Bombay, India. It was found to be inactive for butane dehydrogenation reactions. Therefore,

it was used as support material in the present work.   This material has been designated as I(K) in the text.

TABLE 4.1   CHEMICAL COMPOSITION OF I(K) CATALYST

Component	mol%
Al_2O_3	75.37
Fe_2O_3	13.26
MgO	9.68
Cr_2O_3	1.69

Four compositions of β-bismuth molybdates corresponding to 3 mol, 5 mol, 7 mol and 9 mol per 100 mol I(K) were prepared. The actual chemical compositions of these catalysts are shown in Table 4.2.

TABLE 4.2   CHEMICAL COMPOSITIONS OF BETA BISMUTH MOLYBDATE-I(K) CATALYSTS

Components	mol/100 mol I(K)	3	5	7	9
Al_2O_3 ,	mol%	73.19	72.00	70.43	69.17
Fe_2O_3 ,	"	12.84	12.60	12.38	12.14
MgO ,	"	9.38	9.20	9.04	8.86
Cr_2O_3 ,	"	1.63	1.58	1.57	1.54
$Bi_2O_3 \cdot 2MoO_3$,	"	2.95	4.72	6.58	8.28

Similarly γ -bismuth molybdate with four compositions (i.e. 5, 10, 15 and 20 mol of per 100 mol of I(K)) were prepared. The actual compositions are shown in Table 4.3.

TABLE 4.3 CHEMICAL COMPOSITIONS OF GAMMA BISMUTH MOLYBDATE-I(K) CATALYSTS

mol/100 mol I(K) \\ Components	5	10	15	20
Al_2O_3, mol%	71.80	68.58	65.57	62.82
Fe_2O_3, "	12.60	12.03	11.51	11.02
MgO , "	9.20	8.79	8.40	8.05
Cr_2O_3, "	1.60	1.53	1.46	1.40
$Bi_2O_3 \cdot MoO_3$, "	4.80	9.07 '	13.06	16.71

Another catalyst obtained from M/s. Associated Cement Companies Ltd., Bombay, India and designated as ACC catalyst has also been used in the present study. The chemical composition for this catalyst is presented in Table 4.4.

TABLE 4.4 CHEMICAL COMPOSITION OF ACC CATALYST

Components	mol %
Al_2O_3	77.22
Fe_2O_3	14.46
MgO	4.10
Cr_2O_3	2.73
Bi_2O_3	1.48

4.2 Tap Density

Tap density of catalysts was determined by measuring the weight of a specified volume of catalyst powder packed by gentle tappings. The data are presented in Table 4.5.

TABLE 4.5   TAP DENSITIES OF DIFFERENT CATALYSTS

Catalyst	Tap density, g/cm^3
I(K)	0.977
$Bi_2O_3.2MoO_3$ (β--)	2.481
βI(K) 3mol	1.199
βI(K) 5 mol	1.308
βI(K) 7mol	1.383
β I(K) 9mol	1.432
$Bi_2O_3.MoO_3$ (γ-)	1.760
γI(K) 5mol	1.251
γI(K) 10mol	1.405
γI(K) 15mol	1.563
γI(K) 20mol	1.657
ACC	1.054

4.3 Surface Area

The surface area measurements of the catalysts were carried out by single point BET method with the help of Quanta

Chrome, Model OS-7 (Quanta Chrome Corporation, Greenvale, N.Y. 11548), using N_2 as adsorbent. The results are presented in Table 4.6.

TABLE 4.6   SURFACE AREA VALUES FOR DIFFERENT CATALYSTS

Catalyst	Specific surface area, m^2/g
$Bi_2O_3 \cdot 2MoO_3$ (β-)	2.8
$Bi_2O_3 \cdot MoO_3$ (γ-)	7.6
I(K)	209.4
β I(K) 5mol	7.5
γ I(K) 15mol	25.5

4.4   Thermal Analysis

The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were carried out in order to understand the thermal stability and to confirm the presence of active gradients by their usual phase transitions.   A complex thermoanalytic equipment (Derivatograph, M.O.M., Budapest) was used to carry out these studies. α-Alumina was used as a reference material.   The experiments were conducted in air at atmospheric pressure in the temperature range of 20-800°C with a heating rate of 10°C/min.

DTA thermograms for different catalysts have been given

in Figure 4.1. The DTA curve for pureβ –bismuth molybdate
($Bi_2O_3.2MoO_3$) catalyst exhibits three clear endotherms at
about 595°C, 710°C and 740°C. Similarly three endotherms were
observed in the case of γ–bismuth molybdate ($Bi_2O_3.MoO_3$) catalyst
at about 620°C, 685°C and 700°C. Similar observations have
been reported by Shenoy [15]. All these endotherms may be
attributed to the respective phase transformations. The DTA
thermograms for β I(K) 5 mol and γI(K) 15 mol catalysts also
exhibit endothermic peaks at low temperature of about 120°C
which are due to the dehydration of the catalysts. No signi-
cant endothermic peaks except one (very weak) at about 700°C in
the case of γI(K) 15 mol were observed in the supported catalysts.
The presence of small endothermic peak may be attributed to
the higher concentration (13.06 mol%) of γ–bismuth molybdate
in the catalyst.

TGA thermograms for different catalysts as shown in Fig.
4.2 do not show weight loss for pure β– and pure γ–bismuth
molybdate catalysts. However, the supported catalysts show
weight loss only at about 120°C due to dehydration. The
weight loss was found to be 8.5% in the case of β I(K) 5 mol
and 6.4% in the case of γ I(K) 15 mol catalyst. Beyond 120°C the
weight loss was insignificant upto 800°C.
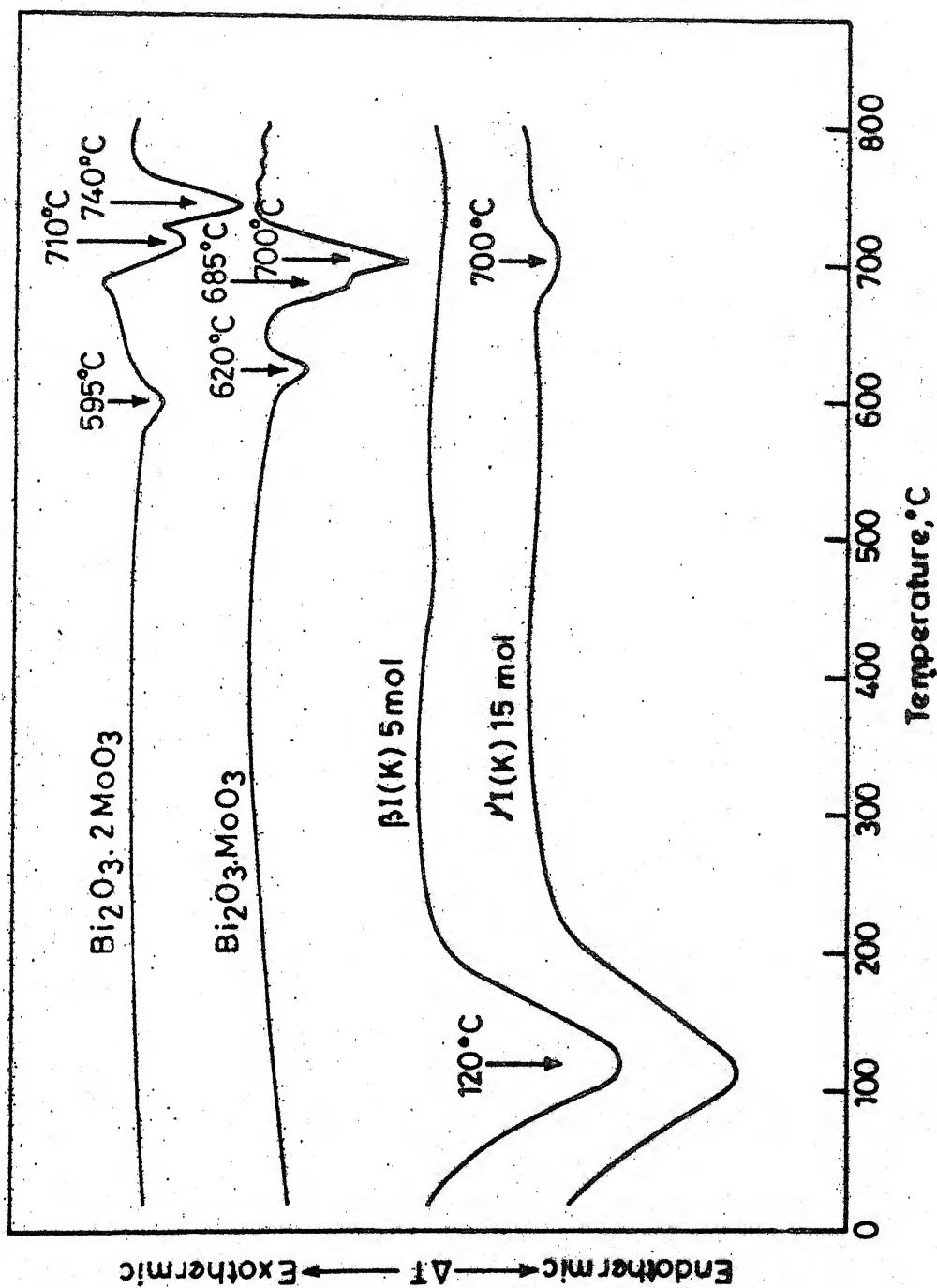
Fig. 4.1 – Differential thermal analysis thermograms of different catalysts.

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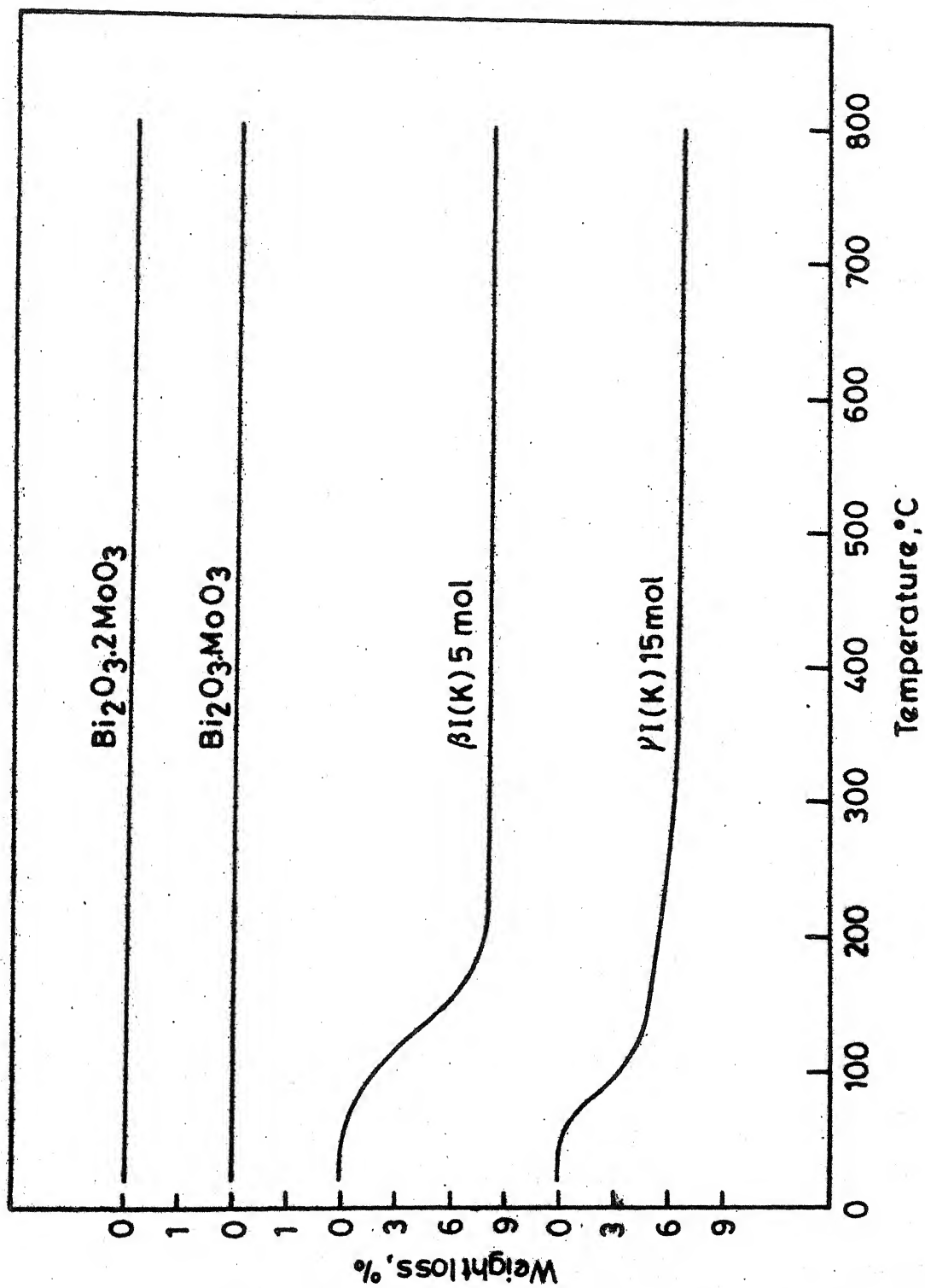
Fig. 4·2 - Thermogravimetric analysis thermograms of different catalysts.

4.5 X-Ray Diffraction Studies

The technique of X-ray diffraction was used to identify the presence of various components and their phases in the pure support and the catalysts. The powdered samples were examined with the help of Seifert Iso-debyeflex 2002 X-ray generator using Seifert MZ III goniometer and diffractometer under following experimental conditions:

Radiation	:	CuKα with Ni filter
Width of receiving slit	:	0.3 mm
Width of scanning slit	:	2 mm
Scanning speed	:	1.2°/min (in 2θ)
Chart speed	:	30 mm/min
Count rate	:	500/s
Time constant	:	10/s

The 'd' values were estimated from the angle of diffraction peaks in usual way. The measured and standard (ASTM file) 'd' values along with peak intensities from various reflections for different catalyst samples are reported in Table 4.7 to Table 4.11. Table 4.7 and Table 4.8 present the data for the pure β- and pure γ-bismuth molybdates respectively. In both the cases prominent reflections match with those reported by other workers [67, 68] (β-bismuth molybdate : monoclinic cell, a = 11.946 $\overset{\circ}{A}$ b = 10.795 $\overset{\circ}{A}$ and c = 11.876 $\overset{\circ}{A}$; γ-bismuth molybdate : Ortho-rhombic cell, a = 5.502 $\overset{\circ}{A}$, b = 16.213 $\overset{\circ}{A}$ and c = 5.483 $\overset{\circ}{A}$).

TABLE 4.7   'd' VALUES OF PURE BETA BISMUTH MOLYBDATE CATALYST

Observed		Standard[67]		hkl
'd' ($\overset{\circ}{A}$)	I/Io	'd' ($\overset{\circ}{A}$)	I/Io	
6.605	6	6.607	4	111
5.902	4	5.906	4	002
—	—	4.885	4	021
4.772	2	4.770	2	211, 112
3.770	4	3.770	4	301
3.186	100	3.187	100	320, 023
—	—	2.979	3	123, 231, 004
2.797	53	2.797	27	303
2.695	38	2.697	13	040
2.191	14	2.191	6	341
—	—	2.173	7	512
—	—	2.049	3	305
1.988	8	1.989	13	600
1.978	58	1.979	14	006
1.944	84	1.944	38	343
1.882	11	1.855	3	602
1.803	2	1.806	2	060
1.687	70	1.687	36	326, 623
1.637	49	1.637	23	360, 063

TABLE 4.7 CONTINUED

Observed		Standard [67]		hkl
'd' (Å)	I/Io	'd' (Å)	I/Io	
1.596	23	1.596	13	640, 046
–	–	1.580	2	362
–	–	1.467	2	625
–	–	1.429	3	065
1.401	14	1.402	6	606
1.347	7	1.349	5	080

Additional 'd' Values

'd' (Å)	I/Io
7.971	6
3.740 (γ-Bi_2O_3)	4
3.456	9
2.624	8
2.475 ($Bi_2O_3 \cdot 3MoO_3$)	3
2.416 (γ-Bi_2O_3)	4
2.265 (γ-Bi_2O_3)	2
1.996 (γ-Bi_2O_3)	8
1.857 (γ-Bi_2O_3)	9
1.544 (γ-Bi_2O_3)	2
1.369 (γ-Bi_2O_3)	4

TABLE 4.8   'd' VALUES OF PURE GAMMA BISMUTH MOLYBDATE CATALYST

Observed		Standard [ASTM 21-102]		hkl
'd'(Å)	I/Io	'd' (Å)	I/Io	
8.090	20	8.090	16	020
4.538	6	4.540	2	021
3.778	10	3.780	4	111
—	—	3.260	2	041
3.149	100	3.150	100	131
2.749	83	2.750	16	200
2.740	83	2.741	18	002
—	—	2.701	16	060
2.603	10	2.604	4	220
—	—	2.597	4	022
2.489	40	2.489	8	151
—	—	2.426	2	112
2.273	14	2.276	4	240
2.270	8	2.270	4	042
—	—	1.957	2	152
1.940	93	1.942	18	202
—	—	1.927	10	260
1.924	15	1.925	18	062
—	—	1.889	2	222
1.780	5	1.783	2	023

TABLE 4.8 CONTINUED

Observed		Standard [ASTM 21-102]		hkl
'd' (Å)	I/Io	'd' (Å)	I/Io	
1.730	7	1.730	2	311
-	-	1.724	2	113
-	-	1.684	2	172
1.655	83	1.656	14	331
1.650	83	1.652	20	133
1.633	47	1.634	18	191
1.575	10	1.577	14	262
1.530	2	1.532	2	351
-	-	1.530	2	153
1.400	5	1.402	2	282

Additional 'd' Values

'd' (Å)	I/Io
3.591 (γ-Bi_2O_3)	5
3.495	3
2.871 ($Bi_2O_3 \cdot 3MoO_3$)	10
2.433	8
2.165 (γ-Bi_2O_3)	3
2.148 (γ-Bi_2O_3)	7
2.111 ($Bi_2O_3 \cdot 3MoO_3$)	3
1.846 ($Bi_2O_3 \cdot 3MoO_3$)	8
1.820 ($Bi_2O_3 \cdot 3MoO_3$)	8
1.742 (γ-Bi_2O_3)	7
1.703 (γ-Bi_2O_3)	7

Some additional very weak reflections were observed in both the cases. These could be attributed to the presence of small proportions of γ-bismuth oxide and α-bismuth molybdate. Existence of such mixed phases have also been reported in the literature [67, 15].

The 'd' values from pure support are given in Table 4.9. Only two weak reflections from (400) and (440) of γ-alumina are visible while the other prominent lines were absent. It indicates that alumina is in mostly pseudo amorphous state. This was also confirmed by electron microscopy studies (Section 4.6). Iron oxide was the second highest component in the support. Majority of reflections matched with α-iron oxide. Only two very very weak reflections from (200) and (220) of MgO and merely one very weak reflection from (104) of Cr_2O_3 could be observed. These reflections correspond to highest peak intensities in ASTM data file. Thus, these weak intensities observed are mainly due to the small proportion of these components (MgO 9.68 mol% and Cr_2O_3 1.69 mol%). Some additional peaks were also observed. Few of them were from ε-Fe_2O_3 and others could not be identified.

Table 4.10 and 4.11 present the data for β I(K) 5 mol and γ I(K) 15 mol catalysts respectively. The 'd' values reported in these tables correspond to 'd' values as obtained from pure support (Table 4.9) and from pure β-and γ-bismuth molybdate

TABLE 4.9   'd' VALUES OF CATALYST SUPPORT, I(K)

Components	Observed		Standard		hkl
	'd'($\overset{\circ}{A}$)	I/Io	'd'($\overset{\circ}{A}$)	I/Io	
γ-Al$_2$O$_3$	-	-	4.560	40	111
[ASTM10-425]	-	-	2.390	80	311
	-	-	2.280	50	222
	1.976	20	1.977	100	400
	1.392	26	1.395	100	440
α-Fe$_2$O$_3$	3.661	33	3.660	25	012
[ASTM13-534]	2.689	100	2.690	100	104
	2.512	91	2.510	50	110
	2.201	35	2.201	30	113
	1.836	51	1.838	40	024
	1.689	64	1.690	60	116
	1.595	16	1.596	16	018
	1.483	36	1.484	35	214
	1.452	38	1.452	35	300
	1.308	22	1.310	20	119
MgO	-	-	2.431	10	111
[ASTM4.0829]	2.105	7	2.106	100	200
	1.487	3	1.489	52	220
Cr$_2$O$_3$	-	-	3.633	75	012
[ASTM 6-0504]	2.668	9	2.670	100	104
	-	-	2.480	95	110
	-	-	1.670	90	116

Additional 'd' Values

'd' (Å)	I/Io
2.197 (ε-Fe_2O_3)	10
2.045	5
2.028	5
1.997	7
1.944 (ε-Fe_2O_3)	8
1.935 (ε-Fe_2O_3)	6
1.919	4
1.593	5
1.449	8
1.419	10
1.410	12
1.401	10

TABLE 4.10   'd' VALUES OF 5 MOL BETA BISMUTH MOLYBDATE PER
100 MOL I(K) SUPPORT

Components	Observed		Standard		hkl
	'd'(Å)	I/Io	'd'(Å)	I/Io	
γ-Al$_2$O$_3$	–	–	4.560	40	111
[ASTM 10-425]	–	–	2.390	80	311
	–	–	2.280	50	222
	1.973	18	1.977	100	400
	1.393	20	1.395	100	440
α-Fe$_2$O$_3$	3.651	22	3.660	25	012
[ASTM 13-534]	2.687	100	2.690	100	104
	2.508	82	2.510	50	110
	1.834	58	1.838	40	024
	1.687	73	1.690	60	116
	2.201	18	2.201	30	113
	1.592	36	1.596	16	018
	1.482	36	1.484	35	214
	1.449	36	1.452	35	300
MgO	–	–	2.431	10	111
[ASTM 4-0829]	2.103	5	2.106	100	200
	1.485	2	1.489	52	220

TABLE 4.10 CONTINUED

Components	Observed		Standard		hkl
	'd'(Å)	I/Io	'd'(Å)	I/Io	
Cr_2O_3	-	-	3.633	75	012
[ASTM 6-0504]	-	-	2.670	100	104
	-	-	2.480	95	110
	-	-	1.670	90	116
$Bi_2O_3.2MoO_3$	-	-	6.607	4	111
[67]	-	-	3.770	4	301
	3.185	36	3.187	100	320, 023
	2.795	18	2.797	27	303
	2.693	8	2.967	13	040
	2.193	3	2.191	6	341
	2.176.	3	2.173	7	512
	-	-	1.989	13	600
	-	-	1.979	14	006
	1.943	20	1.944	38	343
	1.685	13	1.687	36	326, 623
	1.632	10	1.637	23	360, 063
	1.587	5	1.596	13	640, 046
	-	-	1.402	6	606
	-	-	1.349	5	080

Additional 'd' Values

'd'($\overset{\circ}{A}$)		I/I_0
2.625		3
2.263	($\gamma - Bi_2O_3$)	3
2.197	($\varepsilon - Fe_2O_3$)	10
2.024		5
1.942	($\varepsilon - Fe_2O_3$)	8
1.919		6
1.858	($\gamma - Bi_2O_3$)	5
1.595		9
1.408		9
1.399		7

TABLE 4.11   'd' VALUES FOR 15 MOL GAMMA BISMUTH MOLYBDATE
PER 100 MOL I(K) SUPPORT

Components	Observed		Standard		hkl
	'd'($\overset{\circ}{A}$)	I/Io	'd'($\overset{\circ}{A}$)	I/Io	
$\gamma - Al_2O_3$	–	–	4.560	40	111
[ASTM 10-425]	–	–	2.390	80	311
	–	–	2.280	50	222
	1.963	15	1.977	100	400
	1.391	13	1.395	100	440
$\alpha - Fe_2O_3$	–	–	3.660	25	012
[ASTM 13-534]	1.685	49	2.690	100	104
	2.508	20	2.510	50	110
	1.830	16	1.838	40	024
	1.680	28	1.690	60	116
	–	–	2.201	30	113
	1.589	6	1.596	16	018
	1.478	10	1.484	35	214
	1.441	10	1.452	35	300
MgO	–	–	2.431	10	111
[ASTM 4-0829]	2.101	5	2.106	100	200
	1.472	2	1.489	52	222

TABLE 4.11   CONTINUED

Components	Observed		Standard		hkl
	'd' (Å)	I/Io	'd' (Å)	I/Io	
Cr_2O_3	—	—	3.633	75	012
[ASTM 6-0504]	—	—	2.670	100	104
	—	—	2.480	95	110
	—	—	1.670	90	116
$Bi_2O_3 \cdot MoO_3$	8.080	4	8.090	16	020
[ASTM 21-102]	—	—	3.780	4	111
	3.142	100	3.150	100	131
	—	—	2.750	16	200
	2.738	41	2.741	18	002
	—	—	2.701	16	060
	2.487	16	2.489	8	151
	1.937	47	1.942	18	202
	—	—	1.927	10	260
	—	—	1.925	18	062
	1.644	36	1.656	14	331
	1.648	36	1.652	20	133
	1.631	35	1.634	18	191
	1.567	16	1.577	14	262
	—	—	1.402	2	282

Additional 'd' Values

'd'($\overset{\circ}{A}$)		I/Io
3.589	(γ-Bi_2O_3)	5
2.869	($Bi_2O_3 \cdot 3MoO_3$)	10
2.428		8
2.195	(ε-Fe_2O_3)	5
2.146	(γ-Bi_2O_3)	6
2.030		3
1.941		4
1.919	($Bi_2O_3 \cdot 3MoO_3$)	6
1.842		8
1.700		7
1.415		5

(Table 4.7 for β- and Table 4.8 for γ-bismuth molybdate)
including additional lines. The exact matching of measured 'd'
values of β - and γ-bismuth molybdate in pure and supported
state indicates the absence of support-catalyst interactions,
whether chemical or structural. Also it is important to mention
that there was no change in X-ray diffraction patterns for the
spent catalysts in comparison to fresh catalyst indicating good
chemical and structural stabilities.

4.6 Electron Microscopic Studies

The transmission electron microscopy was carried out
mainly to study the structure and state of dispersion of the
active components (bismuth molybdates) on the support.

The powdered catalyst particles were suspended in high
purity acetone with the help of ultrasonic vibrator and were
allowed to settle for about an hour. A drop of each of the
above suspensions was carefully placed over a 200 mesh carbon
coated copper support grid. These grids were examined under a
Phillips EM 301 transmission electron microscope operating at
100 KV with a resolution of better than 10 Å. The gold film
deposited on carbon coated copper grids were used as standard
for electron diffraction work. The electron micrographs and
corresponding electron diffraction patterns were recorded for
each of the catalysts. The 'd' values of these electron
diffraction patterns were estimated using gold diffraction

pattern.

$Bi_2O_3.2MoO_3$ (β-phase) Catalyst

The electron micrographs of pure beta bismuth molybdate catalyst are shown in Figs. 4.3a and 4.3b. Usually globular crystals with occasional appearance of crystals with rectangular cross sections are observed. Most of these appears to be agglomerates. Fig. 4.4a shows the particle size distribution. 70% of particles are found to lie in range of 400-1200 Å.

Fig. 4.3c shows the selected area diffraction patterns of the above catalyst corresponding to micrograph 4.3b. As may be noted from the data given in Table 4.12, the calculated 'd' values are in good agreement with the reported 'd' values of beta bismuth molybdate. It thus confirms that the bismuth molybdate catalyst prepared in this study was in single phase and did not show the presence of other forms. This was also confirmed by X-ray diffraction studies.

TABLE 4.12 INTERPLANER SPACINGS ('d' Values) OF ELECTRON DIFFRACTION CORRESPONDING TO FIGURE 4.3C

'd' (Å),observed	'd' (Å),standard[67]	hkl
3.183	3.187	320,023
2.605	2.697	040
1.940	1.944	343
1.697	1.687	326
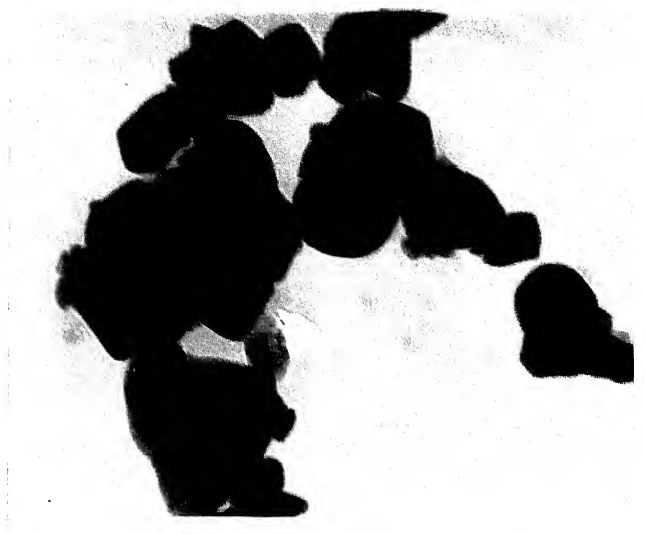
(a) Electron Micrograph
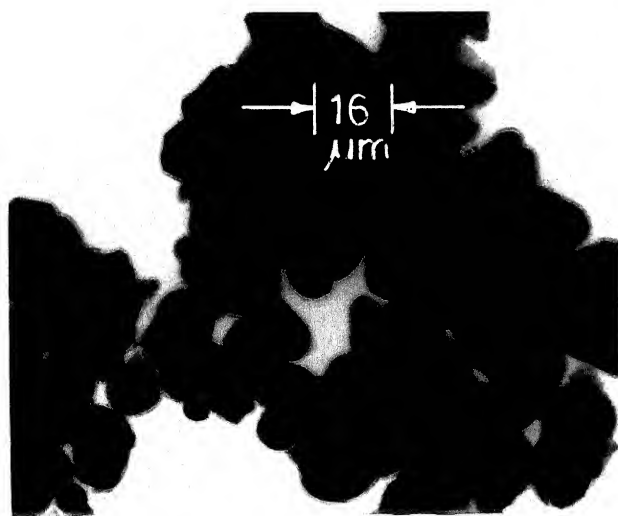
(b) Electron micrograph
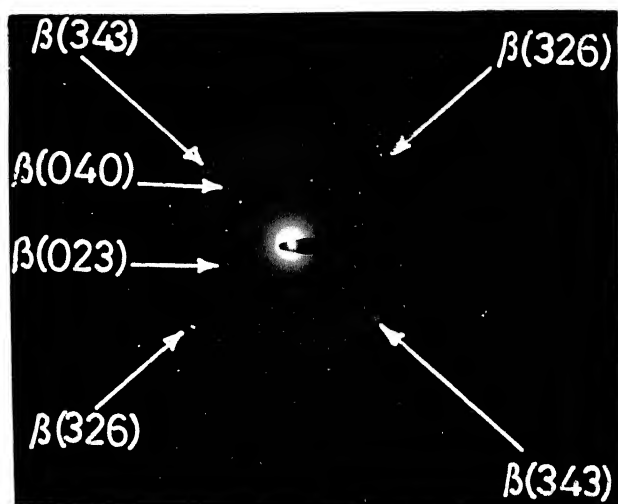
(c) Electron diffraction

Fig. 4.3   Electron microscopic pictures of $Bi_2O_3 \cdot 2MoO_3$ catalyst
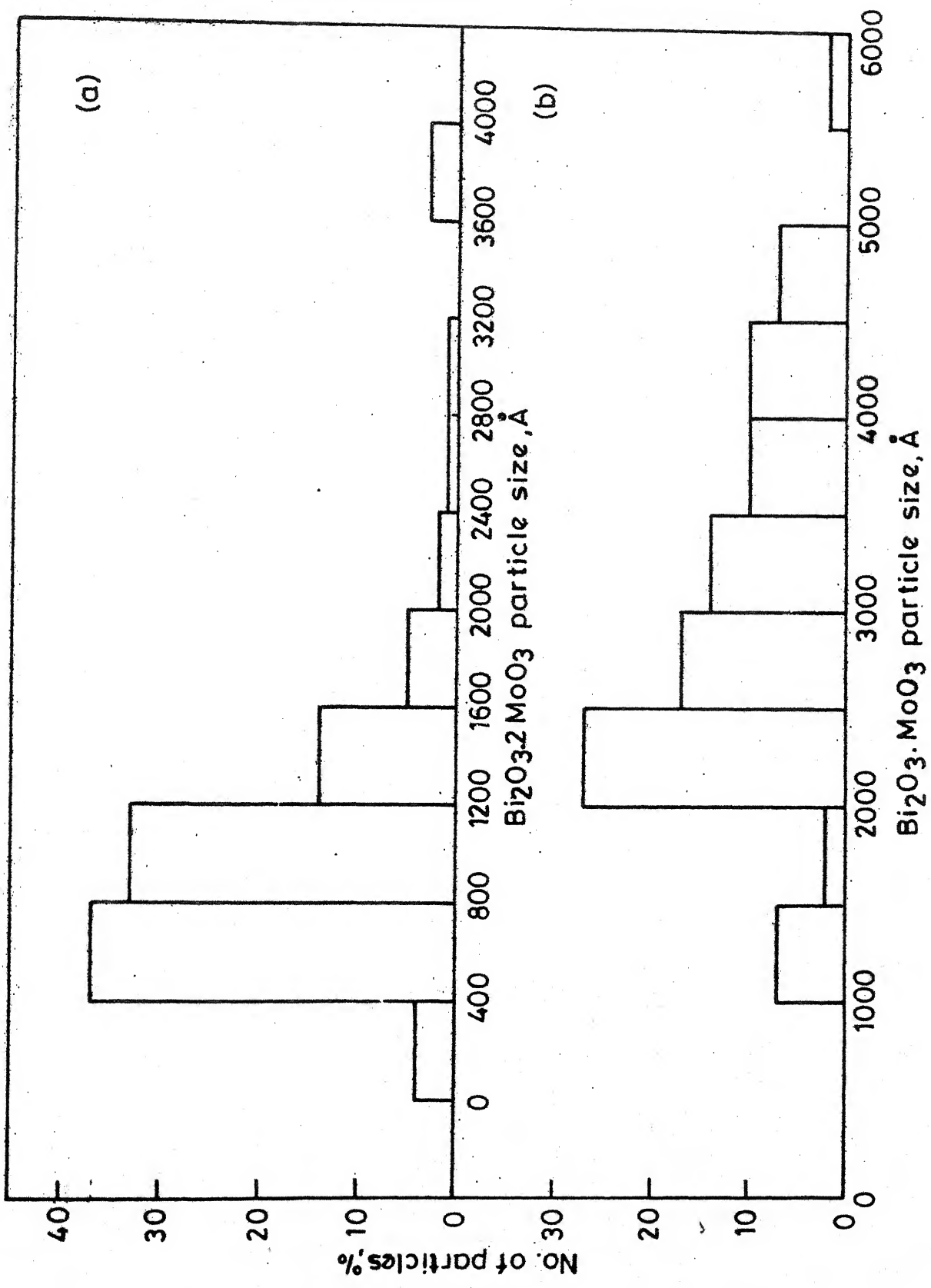
Fig. 4.4 - Particle size distribution of pure β-and pure γ- bismuth molybdate catalysts.

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$Bi_2O_3 \cdot MoO_3$ (γ-phase) Catalyst

The microstructures of pure γ-bismuth molybdate catalyst are shown in Figures 4.5a and 4.5b. The gamma bismuth molybdate crystals appear as elongated prisms with larger grain size in comparison to beta bismuth molybdate crystals. Many of these are intangled to each other. The average particle size distribution is shown in Fig. 4.4b. The 85% particles are found to lie in the range of 2000-5000 Å.

Fig. 4.5c shows the selected area diffraction pattern of the above catalyst corresponding to the micrograph 4.5b. The calculated 'd' values from this pattern are given in Table 4.13. A good agreement with the reported 'd' values corresponding to $Bi_2O_3 \cdot MoO_3$, γ-phase structure (orthorhombic cell, a = 5.502 Å, b = 16.213 Å, and c = 5.483 Å) was observed. No other form of bismuth molybdate was detected.

TABLE 4.13 'd' VALUES CORRESPONDING TO FIGURE 4.5c

'd' (Å), Observed	'd' (Å), Standard [ASTM 21-102]	hkl
3.115	3.15	131
2.206	2.270	042
1.975	1.957	152
1.568	1.577	262

(a) Electron micrograph
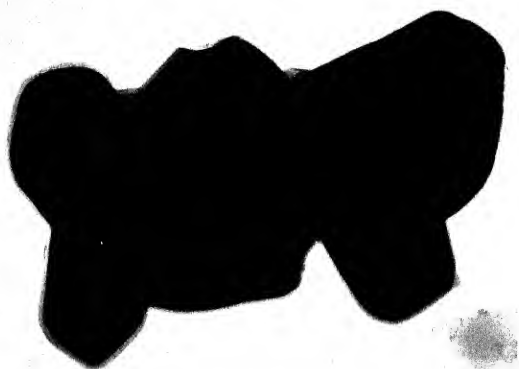
(b) Electron micrograph
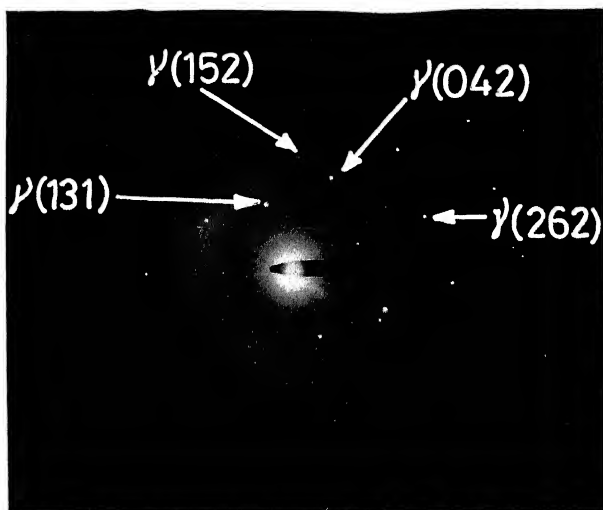
(c) Electron diffraction

Fig. 4.5   Electron microscopic pictures of $Bi_2O_3 \cdot MoO_3$ catalyst

Catalyst Support

The support in the present system consisted of Al_2O_3, Fe_2O_3, MgO and Cr_2O_3 in the molar composition of 75.37%, 13.26%, 9.68 and 1.69%. Electron microscopy of this support was carried out after loading it on a carbon thin film to understand its microstructural behavior. Figure 4.6a is an electron micrograph of the above support. Agglomerates of globular particles are observed. The selected area diffraction pattern of the above is shown in Figure 4.6b. The observed diffraction pattern shows texture. It corresponds to α-iron oxide as indicated from their 'd' values shown in Table 4.14. Alumina is the highest component in the support. However, it did not show any diffraction indicating the presence of alumina in a semi-amorphous state. This was also confirmed by the X-ray diffraction studies. Similarly no diffraction pattern was observed from magnesium and chromium oxides. This may happen also as a result of their minute concentrations in the support.

Supported Catalysts

Bismuth molybdate catalysts impregnated on the support in different proportions as described in Section 4.1 were studied by electron microscopy techniques after usual sample preparations. The observations are presented below.

The electron micrograph and corresponding diffraction for β I(K) 5 mol catalysts are shown in Figs. 4.7a and 4.7b. Two
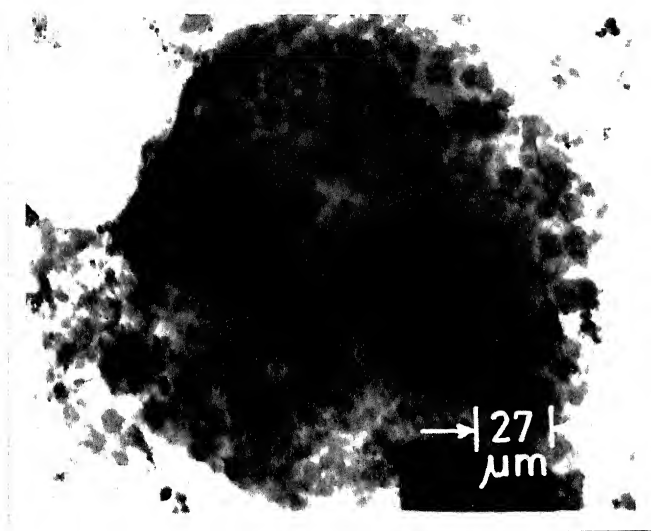
(a) Electron micrograph
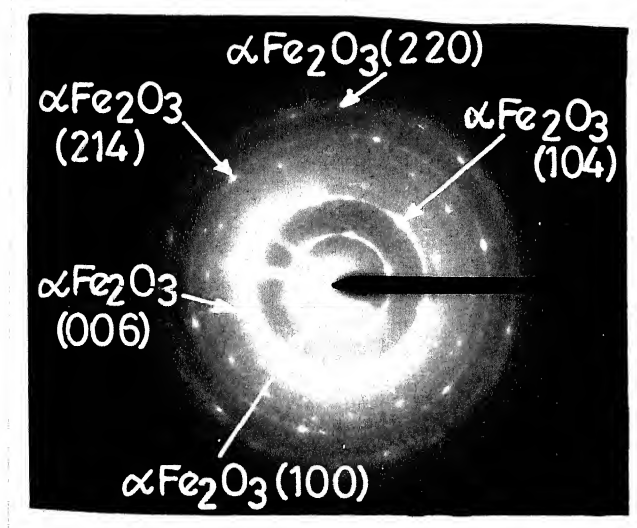
(b) Electron diffraction

Fig. 4.6   Electron microscopic pictures of catalyst support, I(K)
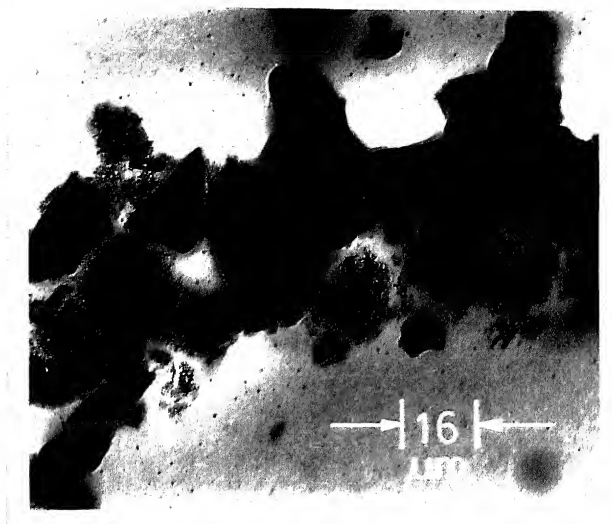
(a) Electron micrograph
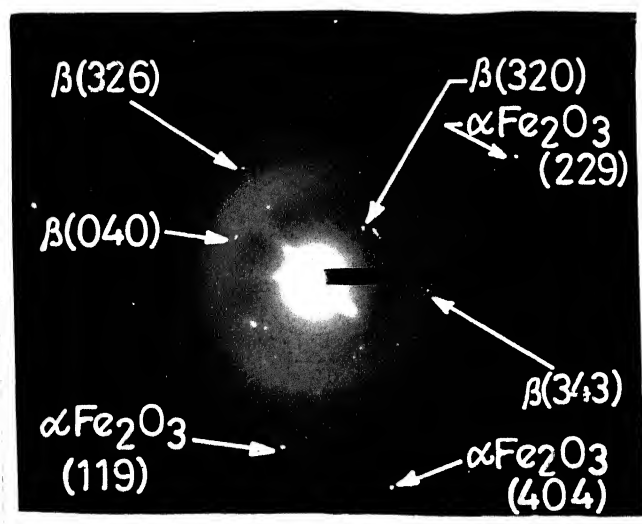
(b) Electron diffraction

Fig. 4.7   Electron microscopic pictures of βI(K) 5 mol catalyst

TABLE 4.14   'd' VALUES CORRESPONDING TO FIGURE 4.6b

'd'(Å), observed	'd'(Å), standard [ASTM 13-534]	hkl
4.398	4.359	100
2.669	2.69	104
2.285	2.285	006
1.7025	1.69	116
1.515	1.484	214
1.310	1.310	119
1.271	1.258	220

types of particles, one consisting of sharp edged particles such as triangular and globular and another type devoid of sharp boundaries are noted from Fig. 4.7a.   The particles without sharp boundaries may be from amorphous alumina.   Both types of particles appear to be coated with beta bismuth molybdate particles which remain unresolved.   The interplaner spacings from corresponding diffraction pattern (Fig. 4.7b) are given in Table 4.15.   While the spots falling on rings correspond to β-bismuth molybdate, the 'd' values from the other intense spots correspond to α-Fe_2O_3.   Quite often, the diffraction from homogeneously coated particles correspond to α-Fe_2O_3 single crystals while diffraction from β-bismuth molybdate is not visible presumably because of absorption in Fe_2O_3 crystals.

Such a situation is shown by electron micrograph in Fig. 4.7c and corresponding diffraction pattern (Fig. 4.7d) which matched with α-Fe$_2$O$_3$ as given in Table 4.16. Another representative micrograph given in Fig. 4.7e shows the support to be homogeneously coated with β-bismuth molybdate. It is interesting to note that unlike pure β-bismuth molybdate which produces big single crystal particles, the supported β-bismuth molybdate gives indistinguishably small particles.

TABLE 4.15   'd' VALUES CORRESPONDING TO FIGURE 4.7b

	'd'(Å), observed	'd'(Å), standard	hkl
Bi$_2$O$_3$.2MoO$_3$	3.183	3.187	320,023
[67]	2.605	2.697	040
	1.940	1.944	343
	1.697	1.687	326
Fe$_2$O$_3$	1.296	1.310	119
[ASTM 13-534]	1.020	1.038	404
	0.975	0.972	229

The observations of electron microscope studies of γ-bismuth molybdate supported catalyst (γI(K) 15 mol) samples prepared in an identical manner as for supported β-bismuth molybdate are shown by representative micrograph and corresponding diffraction pattern in Fig. 4.8a and 4.8b respectively.
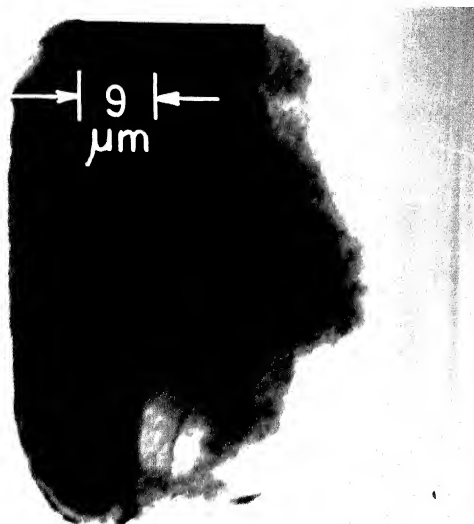
(c) Electron micrograph

(d) Electron diffraction

αFe_2O_3 (104)

αFe_2O_3 (1$\bar{1}$2)

αFe_2O_3 (012)

9 μm

16 μm
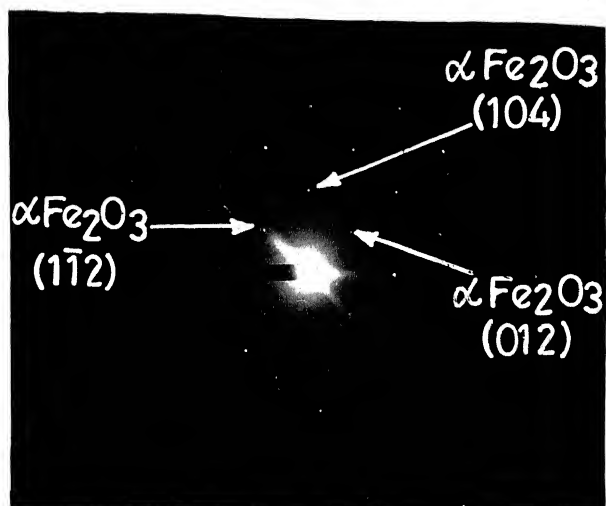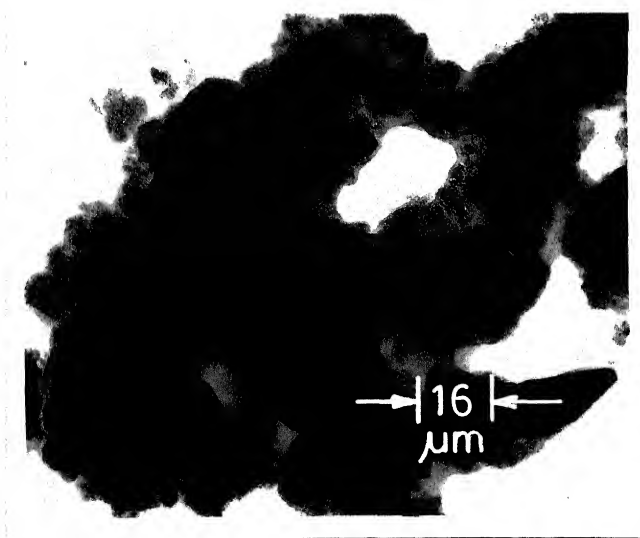
(e)   Electron micrograph

Fig. 4.7   Electron microscopic pictures of β I(K) 5 mol catalyst

(a) Electron micrograph
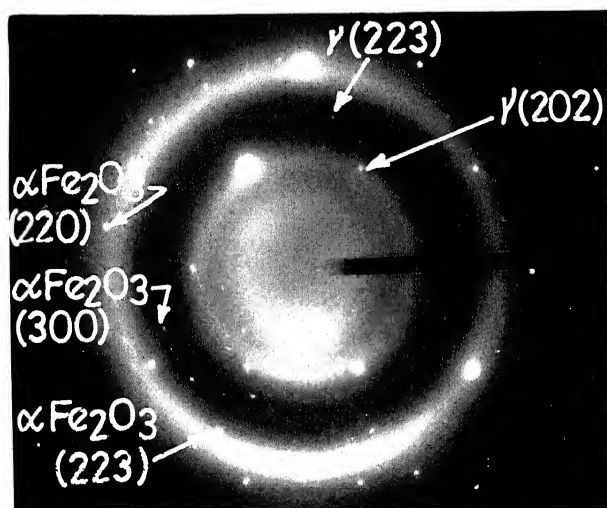
(b) Electron diffraction

Fig. 4.8 Electron microscopic pictures of $\gamma I(K)$ 15 mol catalyst

TABLE 4.16   'd' VALUES CORRESPONDING TO FIGURE 4.7d

'd' (Å), observed	'd' (Å), standard [ASTM 13-534]	hkl
3.679	3.66	012, 1$\bar{1}$2
2.676	2.69	104
1.848	1.86	024
1.745	1.69	116
1.350	1.349	208
1.198	1.189	128

The microstructural features reveal that in this case also the support is homogeneously coated with the catalyst and is quite similar to β-bismuth molybdate. The electron diffraction corresponding to the above micrograph is shown in Fig. 4.8b. The spots forming regular net-work are found to be from α-Fe_2O_3 and rest from the γ-bismuth molybdate as evident from observed interplaner spacings shown in Table 4.17.

TABLE 4.17   'd' VALUES CORRESPONDING TO FIGURE 4.8b

	'd' (Å), observed	'd' (Å), standard	hkl
$Bi_2O_3 \cdot MoO_3$	1.940	1.942	202
[ASTM 21-102]	1.630	1.634	191
	1.485	1.496	223
α-Fe_2O_3	1.418	1.452	300
[ASTM 13-534]	1.295	1.258	220
	1.215	1.213	223

The electron microscopic studies of the catalysts reveal that unsupported pure catalyst materials grow into large size single crystals. Further, the average particle size of β - bismuth molybdate is found to be smaller than γ-bismuth moly-bdate.

The electron microscopic studies of the support consisting of Al_2O_3, Fe_2O_3, MgO and Cr_2O_3 in molar ratio of 75.37%, 13.26%, 9.68% and 1.69%, respectively indicated that alumina is present mostly in amorphous state. The electron diffraction is visible only from α-Fe_2O_3.

The microstructural features as studied from electron microscopy of supported β - and γ-bismuth molybdate seem to be quite similar except in their chemical and crystallographic differences. The support in both the cases is found to be homogeneously coated with the active components. The support appears to be chemically uneffected after impregnation in comparison to the pure catalysts.

4.7 Magnetic Characterization

Fe_2O_3 is another major component of the support (13.26 mol%). This is magnetic in character. In order to investigate the possibility of support-catalyst interactions in fresh and spent catalysts, the magnetization study was carried out. Samples of different catalyst were prepared in the form of short cylinders of 3 mm diameter and 3 mm height. The measurements were accompli-

shed at room temperature using Varian V-7200 series 9" electro-magnet and parallel field vibrating sample magenetometer (Model 150 A PARC, USA). The magnetization curves for support, supported fresh and spent catalysts (for β I(K) 5 mol) are shown in Fig. 4.9 corresponding to one gram equivalent of Fe_2O_3. It is interesting to note that for all the cases the magnetization curves are almost identical indicating either very weak or complete absence of support-catalyst interactions.
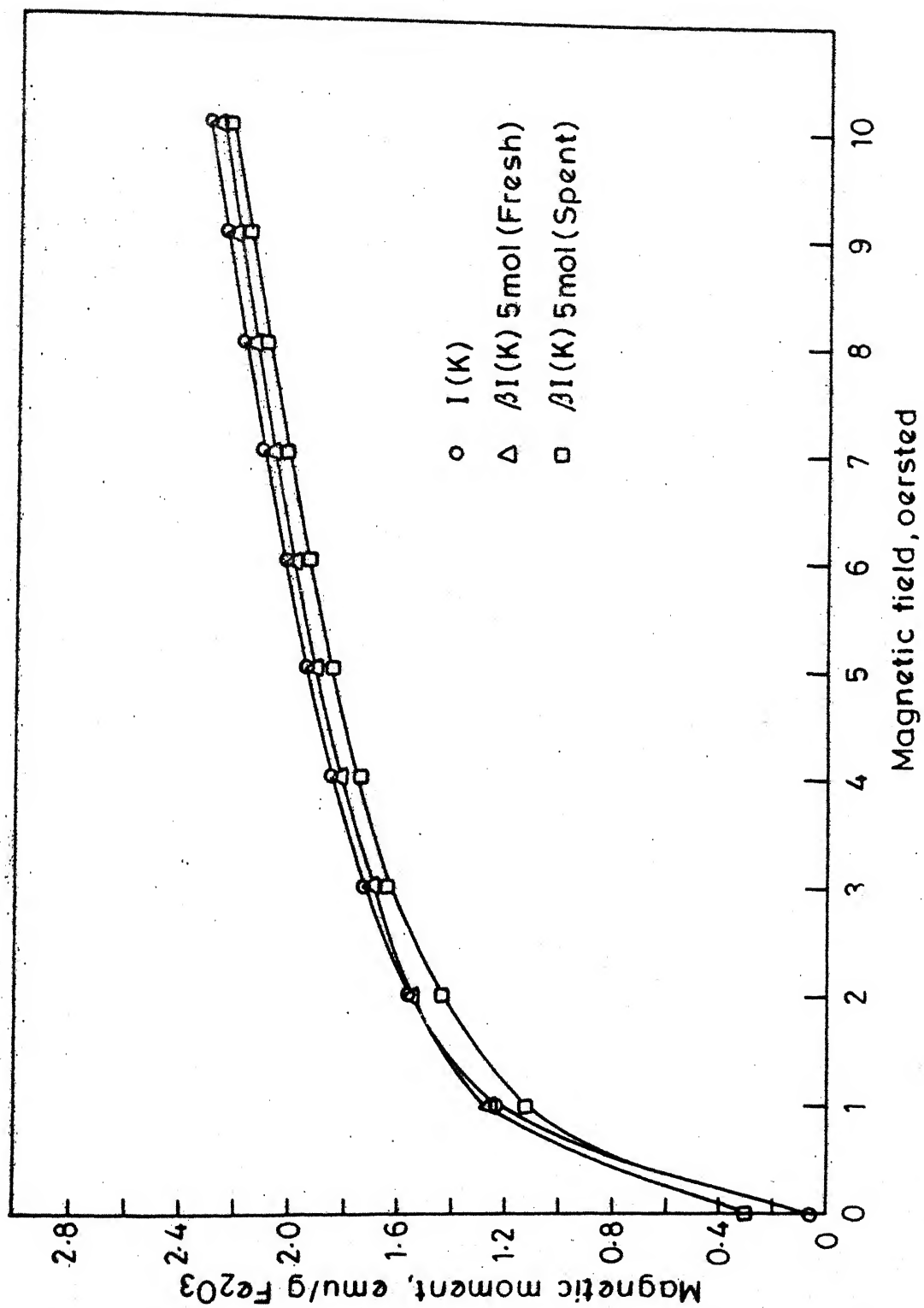
Fig. 4.9 – Magnetic moments of different catalysts.

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CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Reproducibility of the Experimental Results

In order to study the reproducibility of the results, the experiments were repeated five times (runs numbered 1 to 5, details given in Appendix III) under the same conditions. The product distribution data for the specified experimental conditions are given in Table 5.1. The results of conversion, yield and selectivity for these five test runs are given in Table 5.2. The standard deviations for conversion, yield and selectivity are also given in the same table. A good reproducibility of the results is noted.

It may be mentioned that in the presence of excess oxygen, the system acts as a self regenerative type and catalyst fouling does not occur. The theoretical ratio of oxygen to butane ratio for these reactions is 1.0. An oxygen to butane ratio of 1.67 used in these runs contains adequate amount of excess oxygen.

5.2 Mass Transfer Aspects

In the study of heterogeneous catalysis, it is important to check whether the mass transfer resistances are significant. Though the mechanism of the surface catalysis is generally complex; the sequence of the encountered rate steps can be described as follows :

(i) the diffusion of the reacting molecules to the catalyst surface,

(ii) the diffusion of the reacting molecules into the interior of the catalyst particle,

TABLE 5.1   PRODUCT DISTRIBUTION DATA
(on dry basis)

Catalyst weight   :   12.80 g

Active component   : $Bi_2O_3 \cdot 2MoO_3$

Catalyst concentration   :   5 mol/100 mol I(K)

Temperature   :   450°C

W/F   :   2.50 g/(mg mol/min)

Oxygen to butane ratio   :   1.67

Nitrogen to oxygen ratio :   1.60

Run No. / Products, mol%	1	2	3	4	5
Ethylene	0.00	0.11	0.11	0.00	0.00
Propylene	0.00	0.00	0.00	0.00	0.00
n-Butane	14.04	14.04	15.08	14.58	14.02
n-Butene	0.24	0.26	0.22	0.22	0.21
trans-2-Butene	0.32	0.31	0.32	0.29	0.31
cis-2-Butene	0.32	0.32	0.32	0.35	0.32
1,3 Butadiene	1.36	1.44	1.27	1.40	1.50
Methane	0.00	0.00	0.00	0.00	0.00
Carbon dioxide	14.66	16.27	15.06	14.26	15.52
Oxygen	10.03	10.49	12.04	11.78	10.33
Carbon monoxide	3.47	1.17	0.00	1.53	2.21

TABLE 5.2   TEST OF REPRODUCIBILITY

Experimental conditions as given in Table 5.1

Run no. Results	1	2	3	4	5
Conversion of n-butane, mol%	32.51	32.50	27.51	29.89	32.60
Yield(bd), mol%	6.52	6.94	6.09	6.74	7.21
Yield (bute+bd), mol%	10.73	11.27	10.25	10.91	11.28
Selectivity (bd), mol%	20.04	21.35	22.14	22.55	22.12
Selectivity (bute+bd), mol%	32.99	34.66	37.27	36.50	34.62

Standard Deviations

$s_{conversion}$ = 2.02

$s_{yield\ (bd)}$ = 0.38

$s_{yield(bute+bd)}$ = 0.38

$s_{selectivity(bd)}$ = 0.89

$s_{selectivity(bute+bd)}$ = 1.51

(iii) the adsorption of the reactants on the catalyst surface,

(iv) the surface reaction of the reactants to form products,

(v) the desorption of the products from the catalyst surface,

(vi) the diffusion of the products through the interior of the catalyst particle to the external surface of the catalyst and

(vii) the diffusion of the products into the bulk fluid.

To test whether the mass transfer resistances are negligible, one of the simplest methods is to conduct experiments using particles of different sizes of the catalyst under otherwise identical set of conditions. Accordingly, test runs 6 and 7 were conducted and the results are given in Table 5.3. It is noted that the effect of the catalyst particle size on the ultimate results is negligible; indicating, thereby, that the pore diffusional resistances were insignificant and chemical reaction regime is predominant.

5.3 Effect of Mass Flow-rate on Conversion, Yield and Selectivity

Another method to find out whether the reaction is kinetically controlled or controlled by mass transfer, is to vary the mass flow rate and examine its effect on product distribution. Hence the catalyst to gaseous feed flow ratio (W/F) was varied in the range of 0.6–2.6 g catalyst/(mg mol/min). For the reactor

TABLE 5.3   EFFECT OF PARTICLE SIZE OF THE CATALYST ON CONVERSION, YIELD AND SELECTIVITY

Catalyst weight   :   12.80 g

Active component   : $Bi_2O_3 \cdot 2MoO_3$

Catalyst concentration   :   5 mol/100 mol I(K)

Temperature   :   450°C

W/F   :   0.50 g/(mg mol/min)

Oxygen to butane ratio   :   0.80

Nitrogen to oxygen ratio   :   1.60

Particle size of catalyst	Conversion, mol%	Yield(bd), mol%	Yield (bute+ bd), mol%	Selectivity (bd),mol%	Selectivity (bute+bd), mol%
3-6 mesh	22.03	4.76	8.17	21.63	37.11
40-60 mesh	24.20	5.27	8.72	21.75	36.01

size used in the present study this range corresponds to a contact time of about 0.5-2.0 seconds which is normally used in practice. In the typical reactor design used in this study a fixed amount of catalyst charge of 12.80 g was accommodated within the temperature probes. Hence the amount of catalyst charge was not varied. The flow rate of the gaseous feed was varied to obtain the desired range of catalyst to feed ratio.

The experiments were carried out at different oxygen to butane ratios and temperatures. The experimental data have been given in Appendix III. The results have been summarised in Table 5.4 at the specified reaction conditions.

The effect of mass flow rate on conversion has been shown in Fig. 5.1. It is noted that there was negligible effect of mass flow rate on conversion. It means that at all conditions (W/F ratios) an adequate amount of catalyst was present to produce uniform product distributions. Welch et al.[69] found that the mass flow rate had little effect on conversion in the case of .oxidative dehydrogenation of butenes to butadiene.

Fig. 5.2 shows the effect of mass flow rate on the yield of butadiene. The yield of butadiene is found to remain constant with mass flow rate.

Fig. 5.3 shows the effect of mass flow rate on the combined yield of butenes and butadiene. The combined yield was also not

TABLE 5.4   <u>EFFECT OF MASS FLOW RATE ON CONVERSION, YIELD</u>
<u>AND SELECTIVITY</u>

Catalyst   : β I(K)

Weight of catalyst   :   12.80 g

Active component   : $Bi_2O_3 \cdot 2MoO_3$

Catalyst concentration   :   5 mol/100 mol I(K)

Temperature   :   450°C

Oxygen to butane ratio   :   1.67

Nitrogen to oxygen ratio   :   1.60

W/F, g mgmol min Results	0.50	1.00	1.50	1.75	2.00	2.50
Conversion, mol%	33.11	29.20	32.25	30.09	32.15	32.51
Yield (bd), mol%	7.28	7.02	7.48	7.11	7.23	6.52
Yield (bute+bd) mol%	11.89	11.23	12.00	11.36	12.05	10.71
Selectivity (bd), mol%	21.98	24.05	23.19	23.64	22.48	20.04
Selectivity (bute+bd), mol%	35.90	38.47	37.20	37.76	37.47	32.9
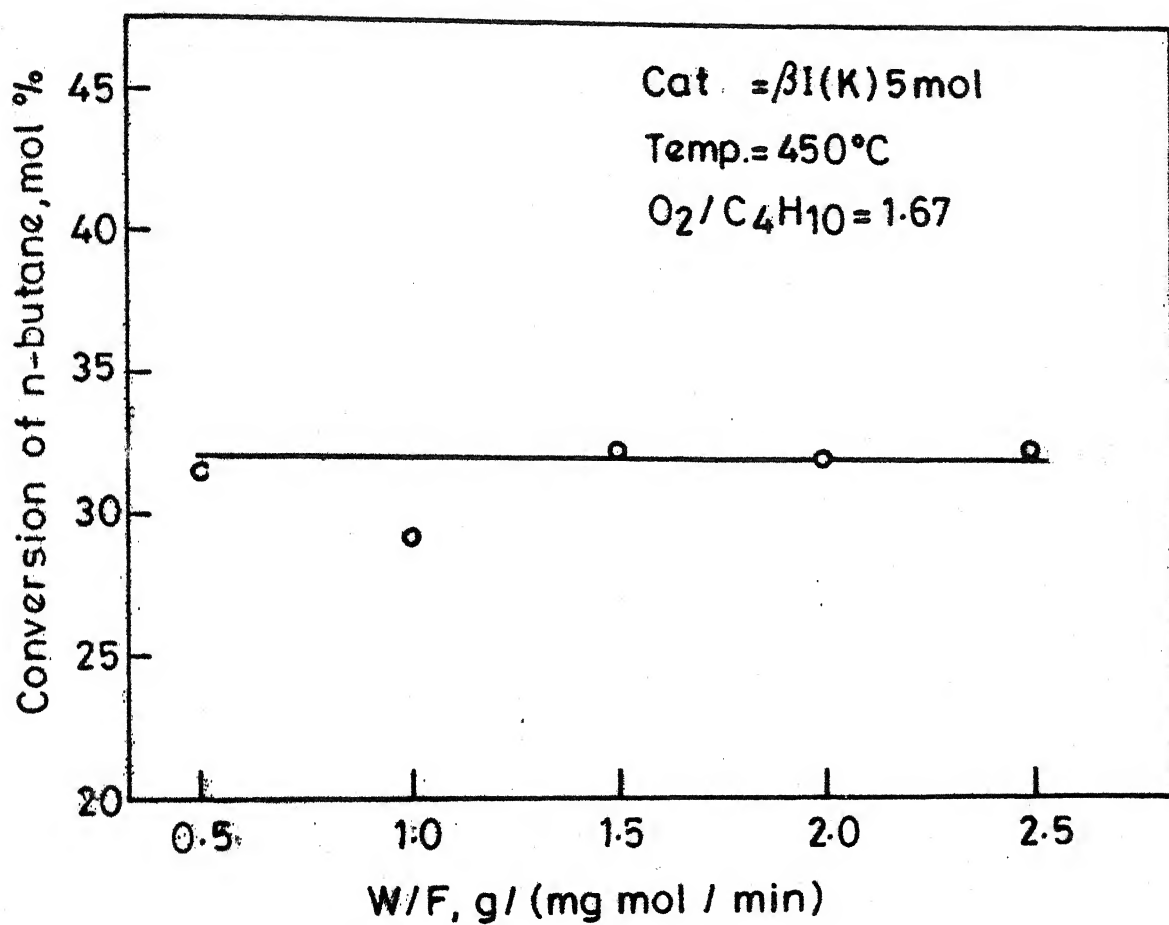
Fig. 5·1 – Effect of mass flow rate (W/F) on conversion of n-butane.
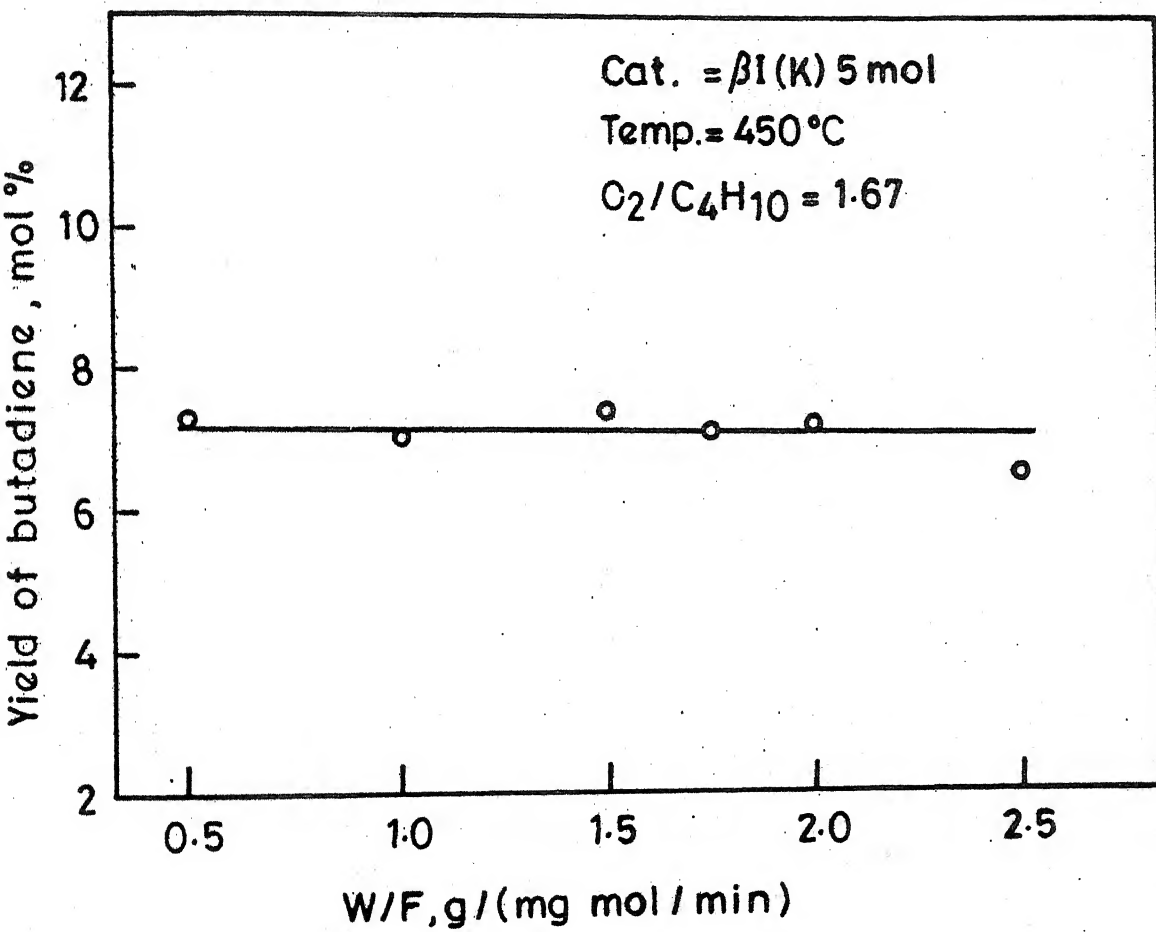
Fig. 5·2 – Effect of mass flow rate (W/F) on yield of butadiene.
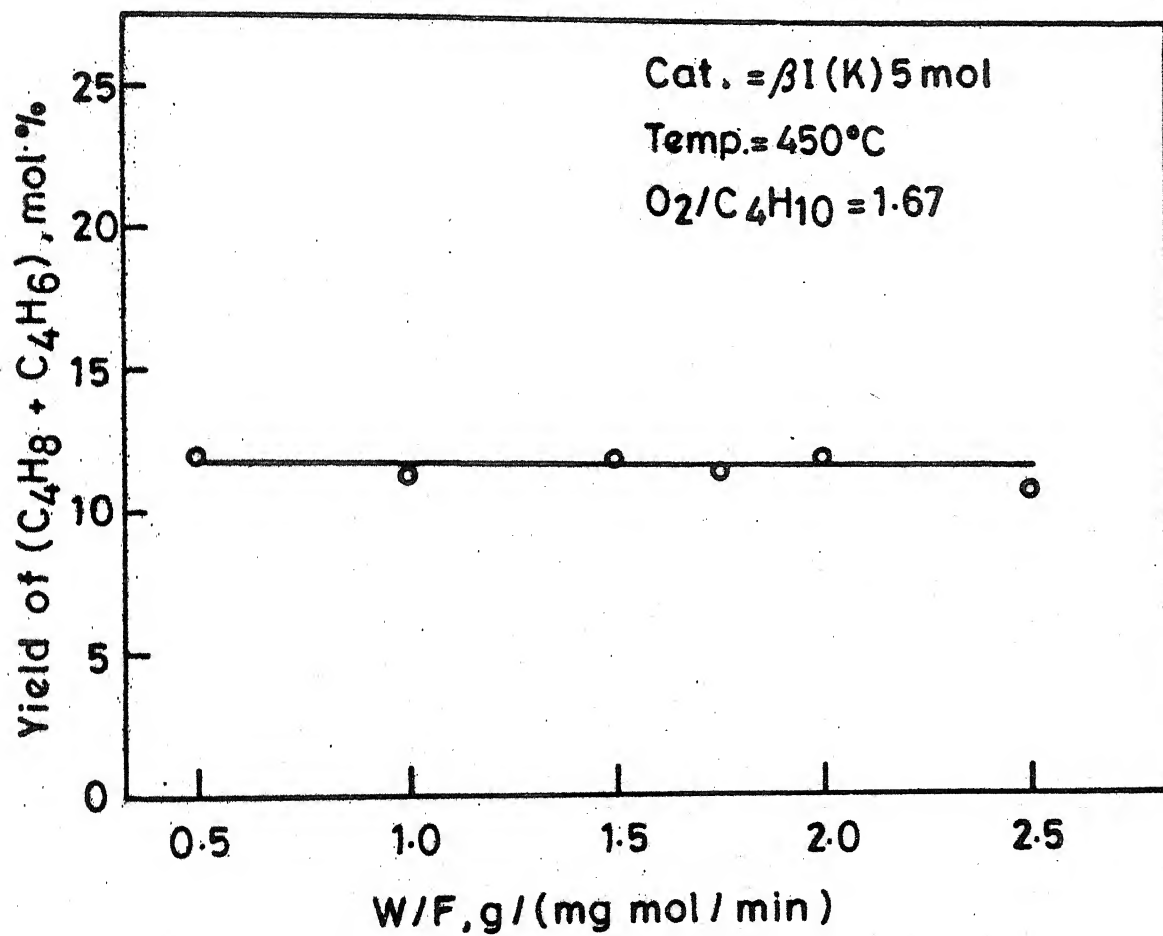
Fig. 5.3 — Effect of mass flow rate (W/F) on yield of (butenes + butadiene).

affected by the mass flow rate. The conversion of butane to butadiene is a consecutive reaction with butenes as intermediate products. It is known that butenes can readily be converted to butadiene. The success of dehydrogenation of the butane to butadiene, therefore, depends greatly on the ease of conversion of butane to butenes.

Fig. 5.4 shows the effect of mass flow rate on the selectivity of butadiene. The selectivity is found to remain constant with mass flow rate.

Fig. 5.5 shows the effect of mass flow rate on the combined selectivity of butenes and butadiene. The selectivity (butenes + butadiene) is also found to remain constant with mass flow rate. These results are in good agreement with the findings of Welch et al. [69] .

Similar observations were made at all O_2/C_4H_{10} ratios and at all temperatures covered in this study

5.4   Effect of Concentration of β -Bismuth molybdate Catalyst on Conversion, Yield and Selectivity

Four catalyst concentrations for β -phase of bismuth molybdate catalyst ($Bi_2O_3.2MoO_3$) were selected for the study of the effect of catalyst concentration. The results (from run Nos. 8 to 27 given in Appendix III) have been summarized in Table 5.5.

For the sake of discussion, the data of Table 5.5 have
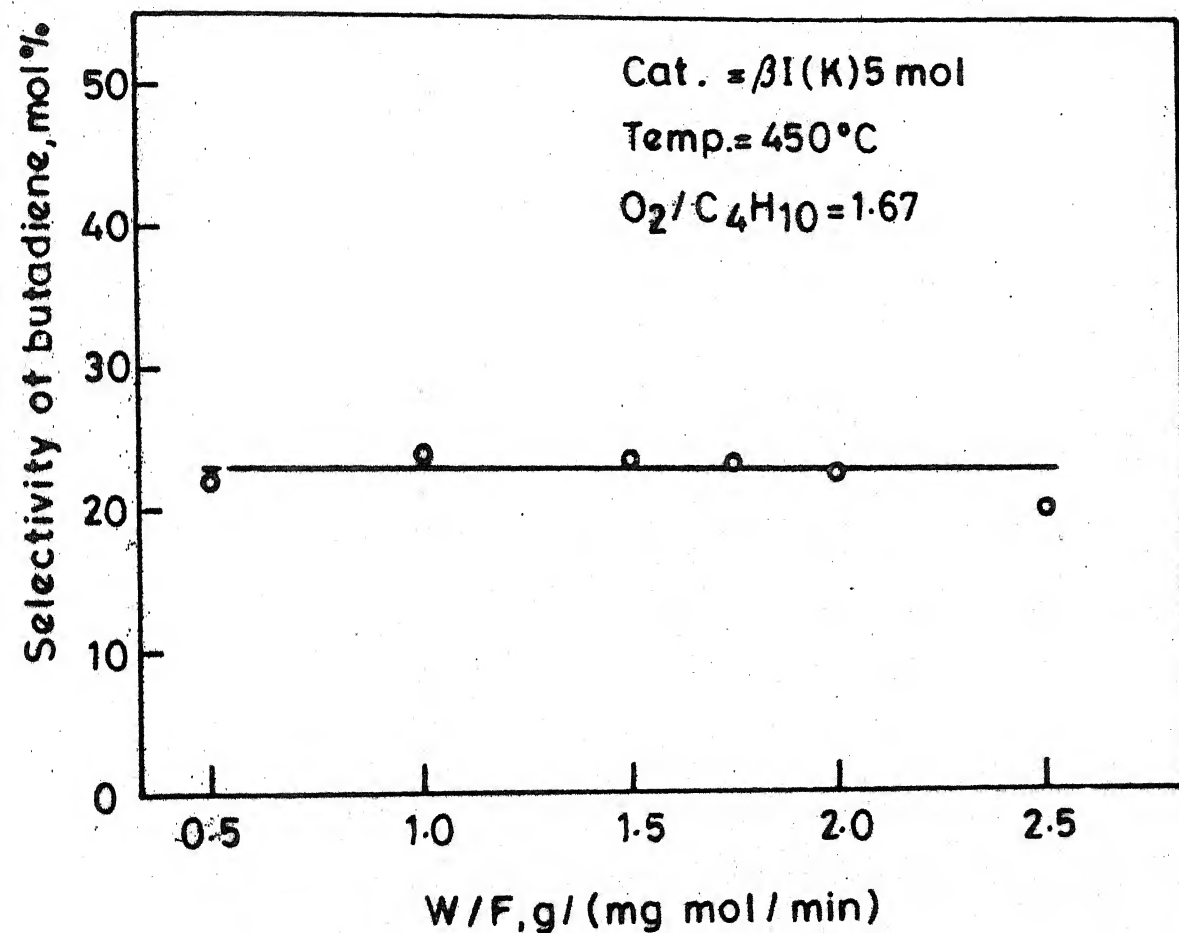
Fig. 5·4 – Effect of mass flow rate (W/F) on selectivity of butadiene.
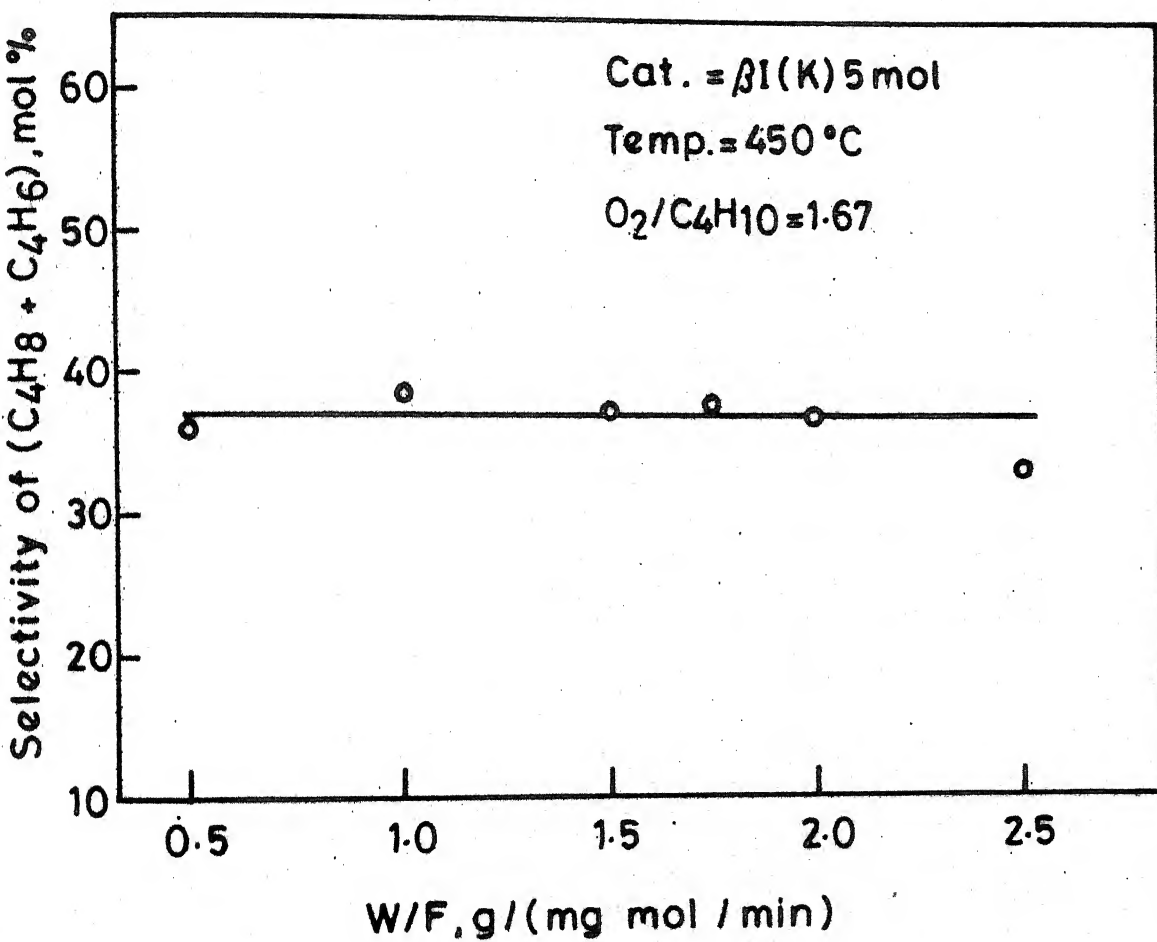
Fig. 5.5 – Effect of mass flow rate (W/F) on selectivity
of (butenes + butadiene).

TABLE 5.5   EFFECT OF CONCENTRATION OF $Bi_2O_3.2MoO_3$ CATALYST
ON CONVERSION, YIELD AND SELECTIVITY

Catalyst   : β I(K)

Catalyst weight   :   12.80 g

Active component   : $Bi_2O_3.2MoO_3$

Temperature   :   450°C

W/F   :   2.00 g/(mg mol/min)

Oxygen to butane ratio   :   1.67

Nitrogen to oxygen ratio   :   1.60

Results / Catalyst concentration mol/100 mol I(K)	Conversion, mol%	Yield (bd), mol%	Yield (bute+ bd), mol%	Selectivity (bd), mol%	Selectivity (bute+bd), mol%
3	29.68	5.26	9.42	17.72	31.75
5	32.15	7.23	12.05	22.48	37.47
7	30.38	6.96	11.02	22.93	36.26
9	28.26	6.00	9.75	21.24	34.51

been represented in Figs. 5.6-5.8.

Fig. 5.6 shows the effect of catalyst concentration on the conversion of n-butane. It is noted that the conversion increased with increase in β-bismuth molybdate concentration upto about 5 mol/100 mol I(K). Thereafter the conversion decreased.

Fig. 5.7 shows the effect of the catalyst concentration on the yield of butadiene. It is observed that the maximum yield occured at the catalyst concentration of 5 mol/100 mol I(K).

Figure 5.8 shows the effect of catalyst concentration on the selectivity of butadiene. The maximum selectivity was found to occur at catalyst concentration of 5 mol/100 mol I(K).

It may be concluded from the above that catalyst concentration of 5 mol/100 mol I(K) gave the optimum results in terms of conversion, yield and selectivity. It is in good agreement with the findings of Shenoy [15] .

5.5 Effect of Concentration of γ-Bismuth molybdate Catalyst on Conversion, Yield and Selectivity

The effect of four different concentrations of γ-bismuth molybdate ($Bi_2O_3.MoO_3$) catalyst on the product distributions have been examined. The data are summarised in Table 5.6. They correspond to run Nos. 28 to 47 given in Appendix III.

Fig. 5.9 shows the effect of catalyst concentration on conversion of n-butane. The optimum conversion is found to occur at 15 mol/100 mol I(K) catalyst concentration.
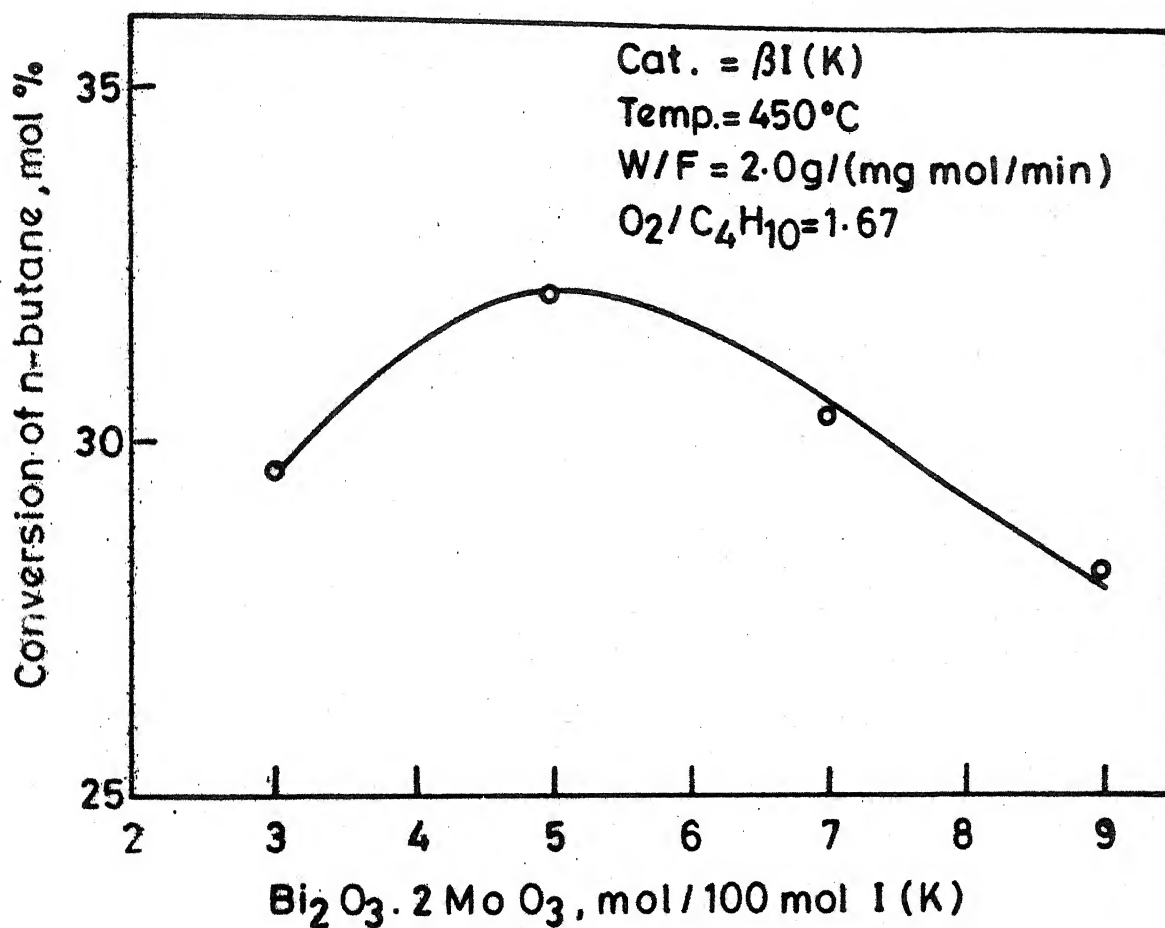
Fig. 5·6 – Effect of concentration of $Bi_2O_3.2MoO_3$
catalyst on conversion of n-butane.
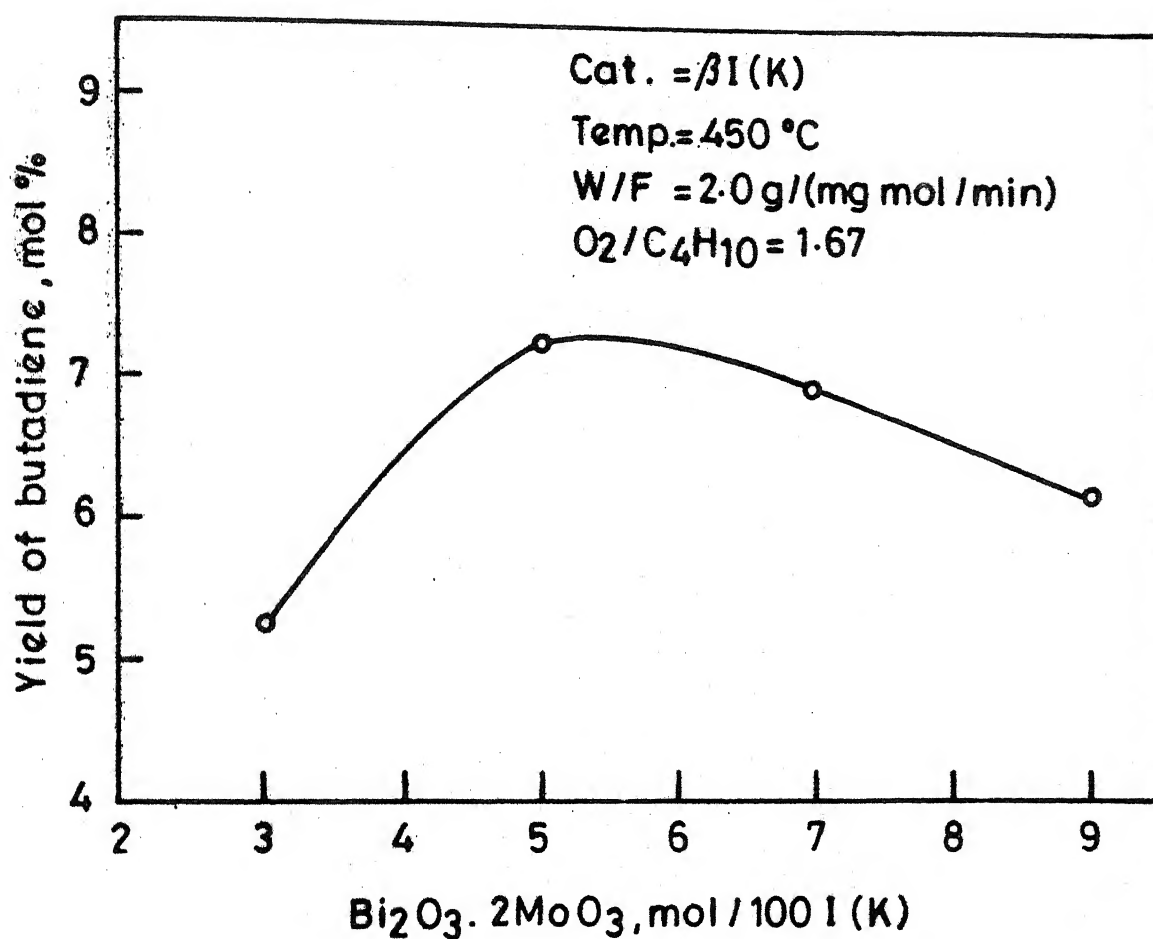
Fig. 5.7 – Effect of concentration of $Bi_2O_3.2MoO_3$ catalyt on yield of butadiene.
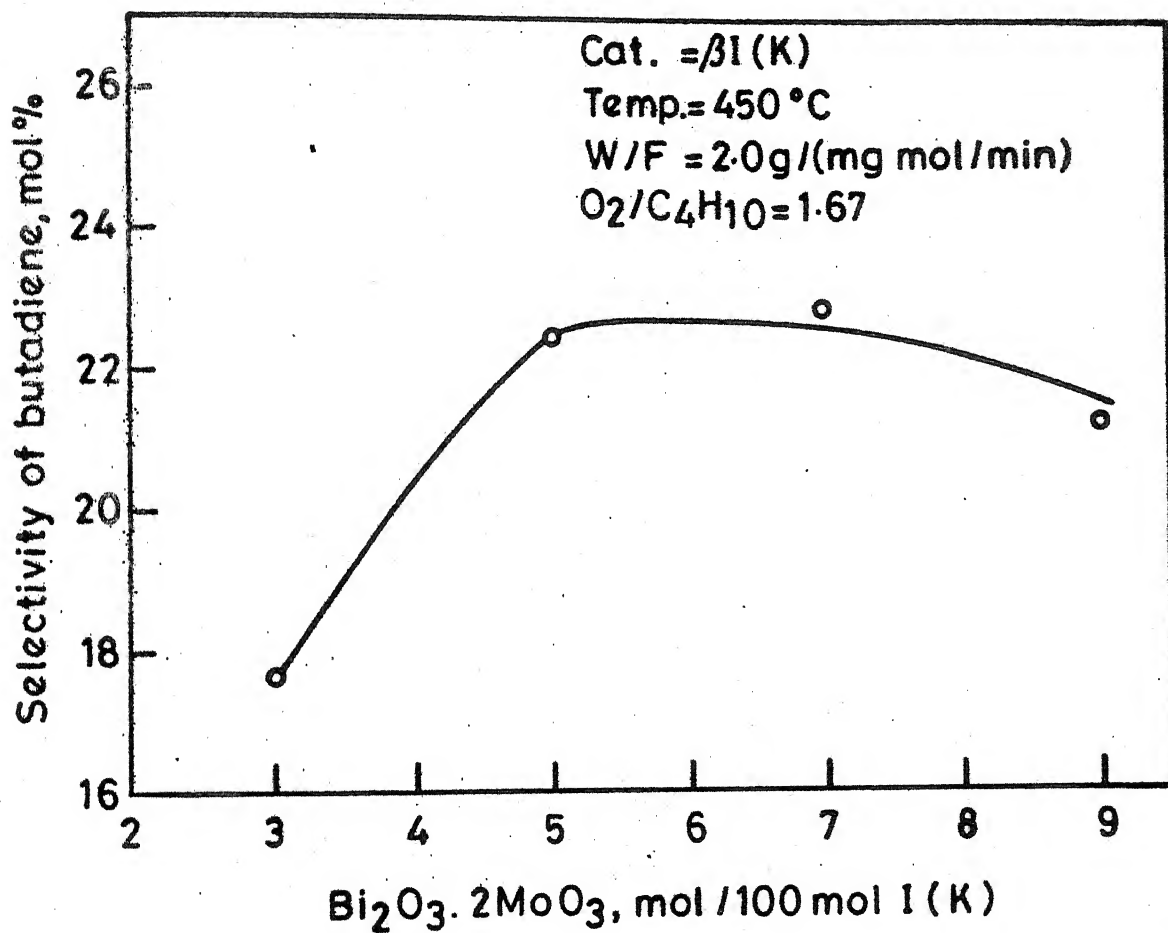
Fig. 5·8 – Effect of concentration of $Bi_2O_3.2MoO_3$ catalyst on selectivity of butadiene.

TABLE 5.6 <u>EFFECT OF CONCENTRATION OF $Bi_2O_3 \cdot MoO_3$ CATALYST ON CONVERSION, YIELD AND SELECTIVITY</u>

Catalyst : $\gamma I(K)$

Catalyst weight : 12.80 g

Active component : $Bi_2O_3 \cdot MoO_3$

Temperature : 450°C

W/F : 2.00 g/(mg mol/min)

Oxygen to butane ratio : 1.67

Nitrogen to oxygen ratio : 1.60

Results Catalyst concentration, mol/100 mol I(K)	Conversion, mol%	Yield(bd), mol%	Yield (bute+bd), mol%	Selectivity(bd), mol%	Selectivity (bute+bd), mol%
5	30.12	3.46	7.20	11.47	23.89
10	34.14	5.21	9.10	15.25	26.66
15	35.10	5.88	9.93	16.76	28.28
20	33.49	5.53	9.45	16.51	28.21
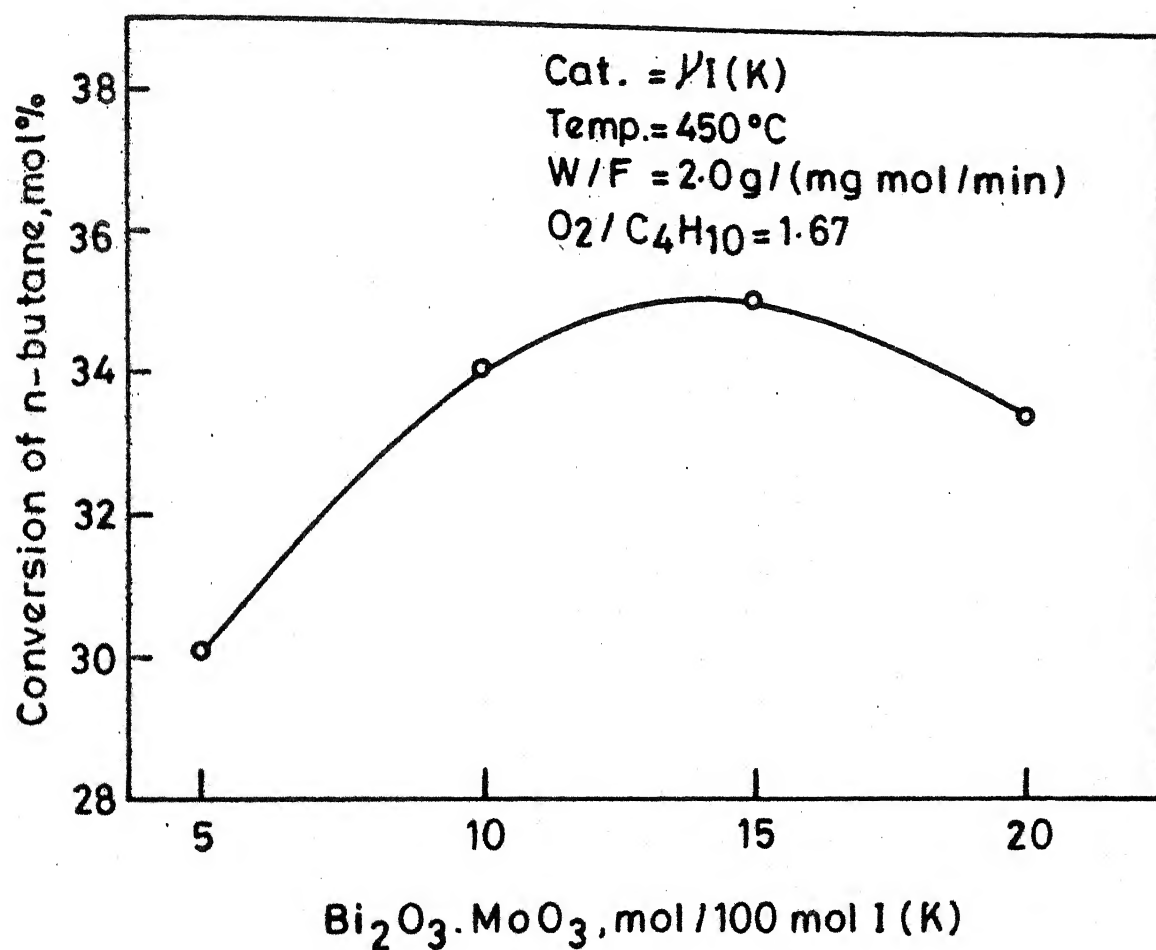
Fig. 5·9 – Effect of concentration of $Bi_2O_3.MoO_3$ catalyst on conversion of n-butane.

Figure 5.10 shows the yield of butadiene with respect to catalyst concentration. The optimum is found to occur at 15 mol/100 mol I(K) catalyst concentration.

Fig. 5.11 shows the effect of catalyst concentration on the selectivity of butadiene. In this case also the optimum occurs at 15 mol/100 mol I(K) catalyst concentration.

It may be concluded from the above observations that the γ-bismuth molybdate has its maximum activity and selectivity at catalyst concentration of 15 mol/100 mol I(K). Shenoy [15] also observed similar behaviour.

5.6 Comparision of Beta and Gamma Phases of Bismuth molybdate Catalysts

It is desirable to compare the activity and selectivity of two phases of bismuth molybdate under the same conditions. The experimental results have been summarised in Table 5.7. It is noted from table that β-phase is more ~~effective~~ active and selective than γ-phase in all respects. This is in close agreement with the observations of Shenoy [15].

5.7 Comparison with ACC Catalyst and Selection of the Catalyst

An ACC catalyst containing bismuth oxide was procured for a comparative study. The chemical composition of this catalyst has been given in Section 4.1. The results obtained for ACC catalyst have been compared with those β- and γ-phases of bismuth molybdate catalysts in Table 5.8. The results for ACC
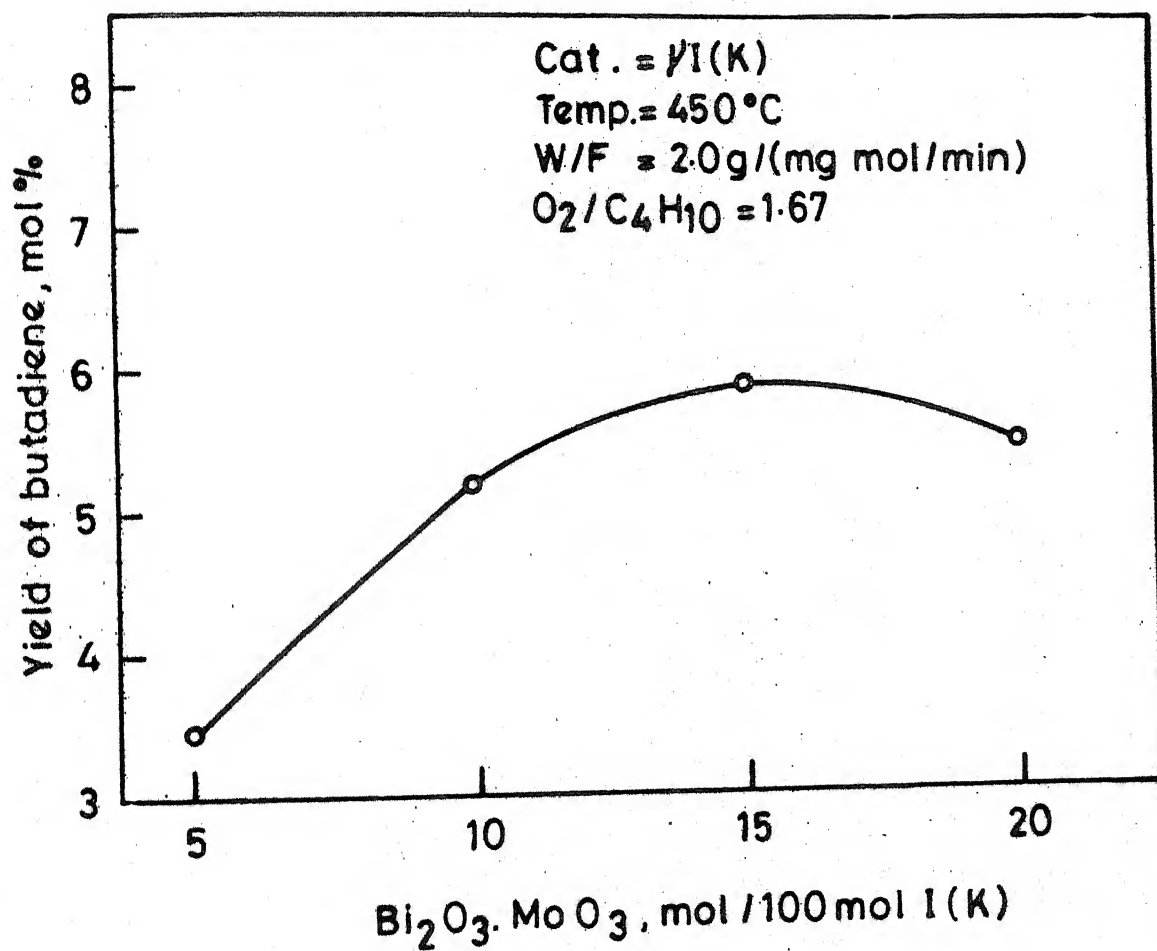
Fig. 5.10– Effect of concentration of $Bi_2O_3 \cdot MoO_3$ catalyst on yield of butadiene.
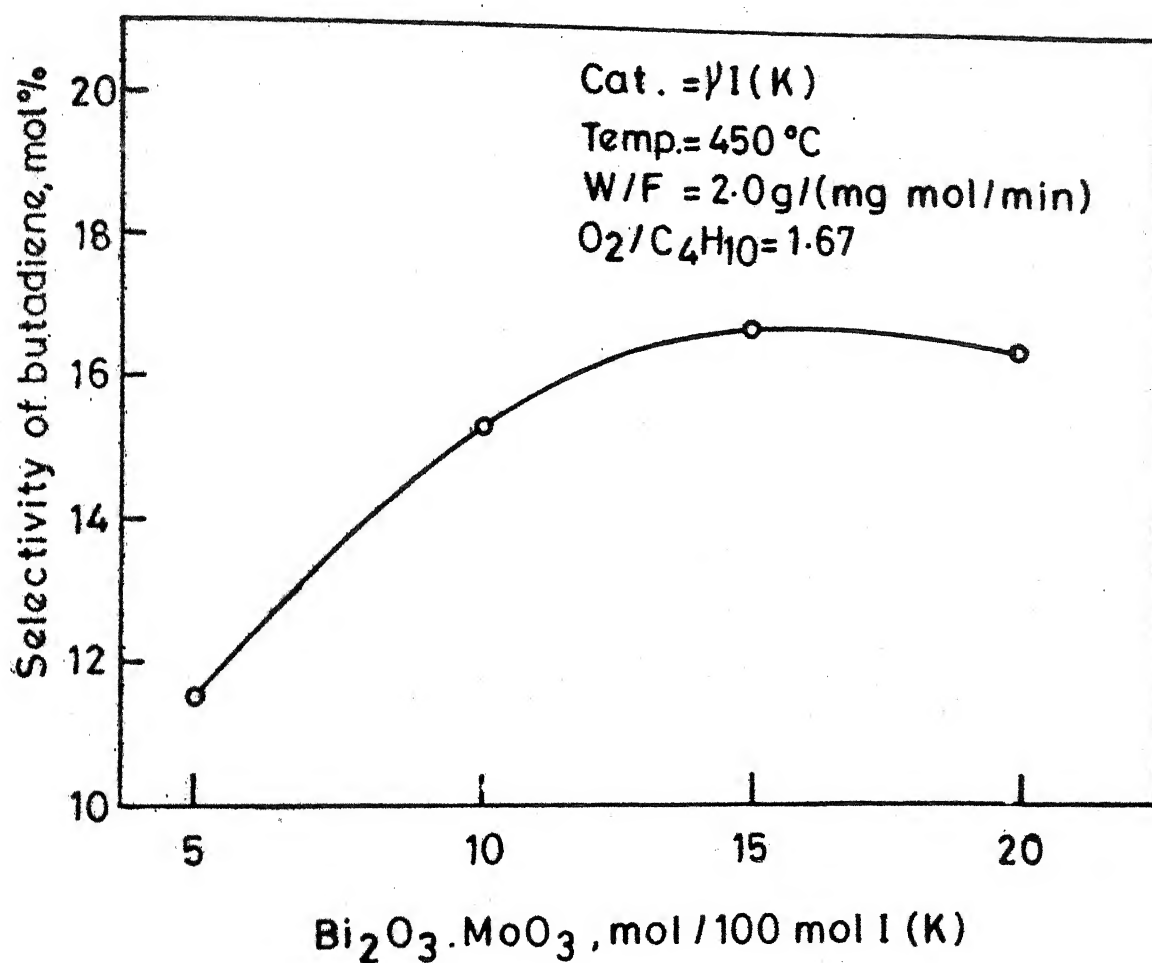
Fig. 5.11 – Effect of concentration of $Bi_2O_3.MoO_3$ catalyst on selectivity of butadiene.

TABLE 5.7   COMPARISON OF BETA AND GAMMA PHASES OF BISMUTH MOLYBDATE CATALYSTS

Catalyst weight : 12.80 g

Catalyst concentration :: 5 mol bismuth molybdate/100 mol I(K)

Temperature :: 450°C

Oxygen to butane ratio :: 1.67

Nitrogen to oxygen ratio ; 1.60

W/F g/(mgmol/min)	β I(K) 5 mol					γ I(K) 5 mol				
	Conversion, mol%	Yield (bd), mol%	Yield (bute+bd), mol%	Selectivity (bd), mol%	Selectivity (bute+bd), mol%	Conversion, mol%	Yield (bd), mol%	Yield (bute+bd), mol%	Selectivity (bd), mol%	Selectivity (bute+bd), mol%
1.00	29.20	7.02	11.23	24.05	38.47	29.13	3.47	7.11	11.92	24.39
1.50	32.25	7.48	12.00	23.19	37.21	30.80	3.33	6.74	10.81	21.88
1.75	30.15	7.11	11.36	23.59	37.69	30.35	3.40	7.20	11.21	23.71
2.00	32.15	7.23	12.05	22.48	37.47	30.12	3.46	7.20	11.47	23.89
2.50	32.51	6.52	10.73	20.04	32.99	28.47	3.38	7.06	11.88	24.81

TABLE 5.8 COMPARISON OF CATALYST PERFORMANCE FOR SELECTION OF THE BEST CATALYST

Catalyst weight : 12.80 g	Temperature	: 450°C
Oxygen to butane : 1.67 ratio	Nitrogen to oxygen ratio	: 1.60

W/F,g/(mg mol/min) Catalysts		1.00	1.50	1.75	2.00	2.50
β I (K) 5 mol	Conversion, mol%	29.20	32.25	30.15	32.15	32.51
	Yield (bd), mol%	7.02	7.48	7.11	7.23	6.52
	Yield (bute+bd), mol%	11.23	12.00	11.36	12.05	10.73
	Selectivity (bd), mol%	24.05	23.19	23.59	22.48	20.04
	Selectivity (bute+bd), mol%	38.47	37.21	37.69	37.47	32.99
γ I(K)15 mol	Conversion, mol%	35.26	35.85	35.44	35.10	34.35
	Yield(bd), mol%	5.75	5.40	6.16	5.88	5.81
	Yield(bute+bd), mol%	9.99	10.62	9.83	9.93	9.84
	Selectivity(bd) mol%	16.30	15.07	17.38	16.76	16.91
	Selectivity (bute+bd),mol%	28.33	29.61	27.73	28.28	28.64
ACC	Conversion, mol%	24.53	27.18	25.50	25.26	26.34
	Yield (bd), mol%	3.46	3.42	3.75	3.60	3.49
	Yield(bute+bd), mol%	8.13	7.95	7.73	8.11	8.40
	Selectivity (bd),mol%	14.09	12.59	14.72	14.26	13.26
	Selectivity (bute+bd),mol%	33.14	29.24	30.33	32.10	31.90

catalyst correspond to run numbers 48 to 52 given in Appendix III.

Fig. 5.12 shows the conversions obtained with different catalysts. The ACC catalyst was found to give lower conversion in comparison to βI(K) and γI(K) catalysts. The ACC catalyst does not contain MoO_3 which is reported to be responsible for the higher activity of bismuth molybdate catalysts.

Fig. 5.13 shows the yield of butadiene obtained from different catalysts. The β I(K) catalyst gave the highest yield.

Fig. 5.14 shows the selectivity of butadiene obtained with different catalysts. The highest selectivity was obtained with β I(K) catalyst.

It becomes clear from the above comparative study that β I(K) 5 mol is the best catalyst. It may also be noted that the mass flow rate had no effect on conversion, yield and selectivity for all the three catalysts. This confirms that the diffusional factors were absent and the kinetics was controlling the reaction rates. Hence βI(K) 5 mol catalyst was selected for further studies on the effect of temperature & oxygen to butane ratio on product distribution.

5.8 Effect of Temperature on Conversion, Yield and Selectivity

At temperatures lower than 400°C, the oxygenated products like alcohols are reported to be formed in preference to dehydro-genated products [70] . Above 500°C the bismuth molybdate
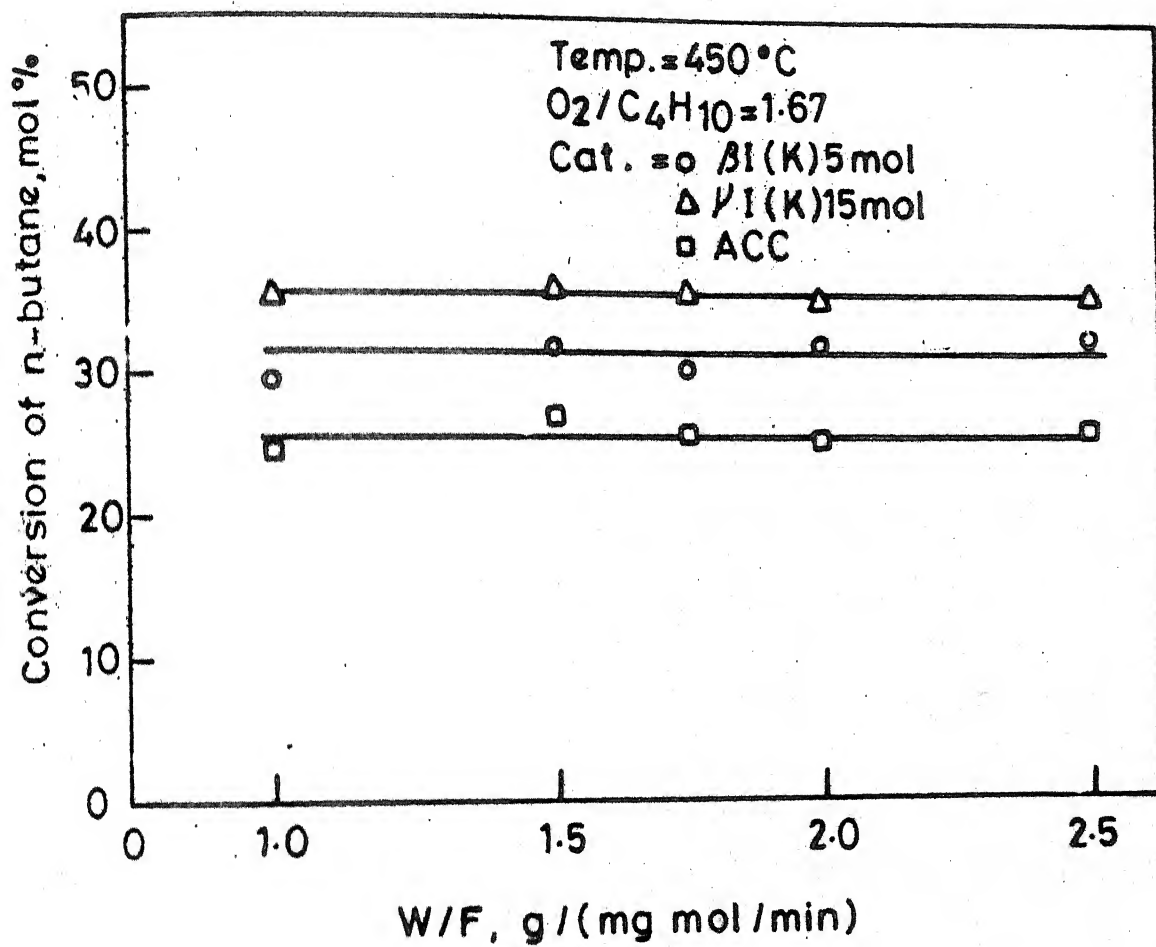
Fig. 5·12 – Conversion of n-butane over different catalysts.
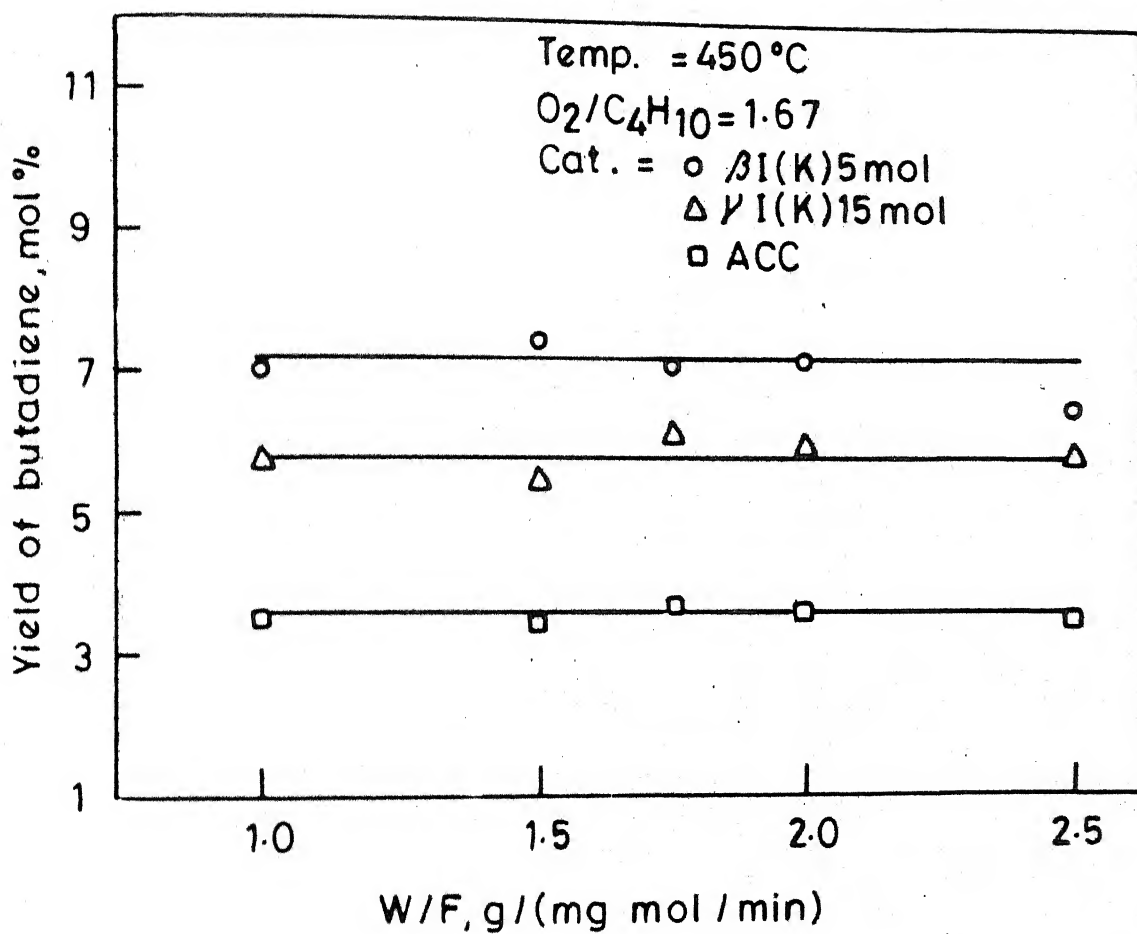
Fig:5.13 - Yield of butadiene over different catalysts.
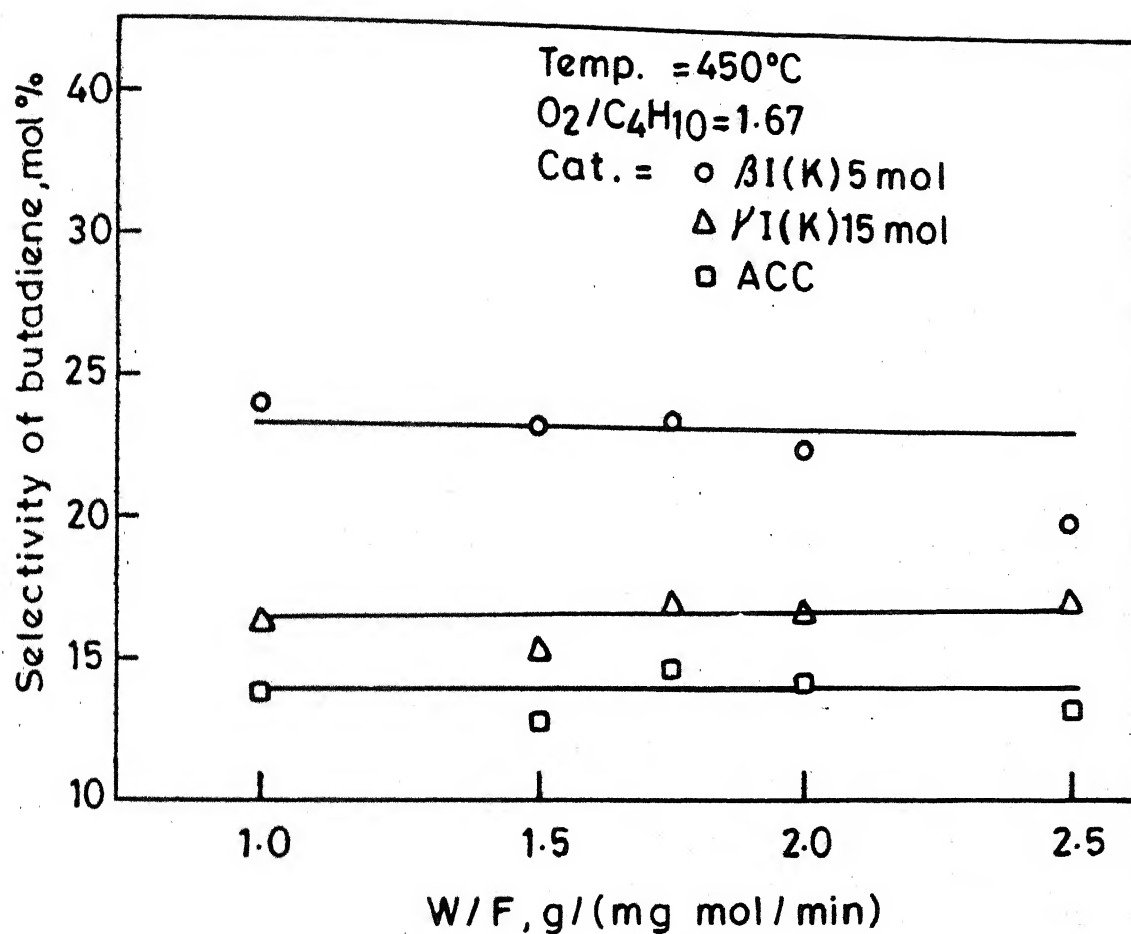
Fig. 5·14 – Selectivity of butadiene over different catalysts.

catalysts tend to loose their activity[70] . Moreover, cracking and secondary reactions become more predominant at higher temperatures. Hence, the experiments were conducted between 400-500°C at different oxygen to butane ratios. The experimental observations have been reported in Appendix III (onward to run No. 52). The results at specified conditions have been summarised in Table 5.9.

Fig. 5.15 shows the effect of temperature on the conversion of n-butane. It is noted that the increase in conversion was slow upto about 450°C and then it increased rapidly.

Fig. 5.16 shows the effect of temperature on the yield of butadiene. The yield of butadiene increased from about 2 mol% at 400°C to about 5.2 mol% at 500°C with its maximum value of about 7.5 mol% at 450°C. A per pass yield of butadiene of about 7.5 mol%, beginning from n-butane, is encouraging.

The effect of temperature on combined yield of butenes and butadiene has been shown in Fig. 5.17. The yield is found to increase upto about 450°C and decrease, thereafter, slowly.

The effect of temperature on the selectivity of butadiene has been shown in Fig. 5.18. The selectivity is found to vary from about 6 mol% at 400°C to about 12.5 mol% at 500°C with a maximum of about 23 mol% at 450°C.

The effect of temperature on combined selectivity of butenes and butadiene has been shown in Fig. 5.19. The combined

TABLE 5.9　EFFECT OF TEMPERATURE ON CONVERSION, YIELD AND SELECTIVITY

Catalyst : β I(K)

Weight of catalyst : 12.80 g

Active component : $Bi_2O_3 \cdot 2MoO_3$

Catalyst concentration : 5 mol/100 mol I(K)

W/F, mg mol/min : 1.50

Oxygen to butane ratio : 1.67

Nitrogen to Oxygen ratio : 1.60

Temperature, °C / Results	400	425	440	450	460	475	500
Conversion, mol%	30.79	31.13	31.13	32.25	34.18	36.74	41.63
Yield(bd), mol%	1.86	4.83	6.47	7.48	6.87	6.53	5.17
Yield(bute+bd), mol%	4.85	9.08	11.00	12.00	12.33	11.26	10.06
Selectivity (bd), mol%	6.06	15.53	20.79	23.19	20.08	17.78	12.42
Selectivity (bute+bd), mol%	15.76	29.17	35.33	37.20	36.09	30.65	24.16
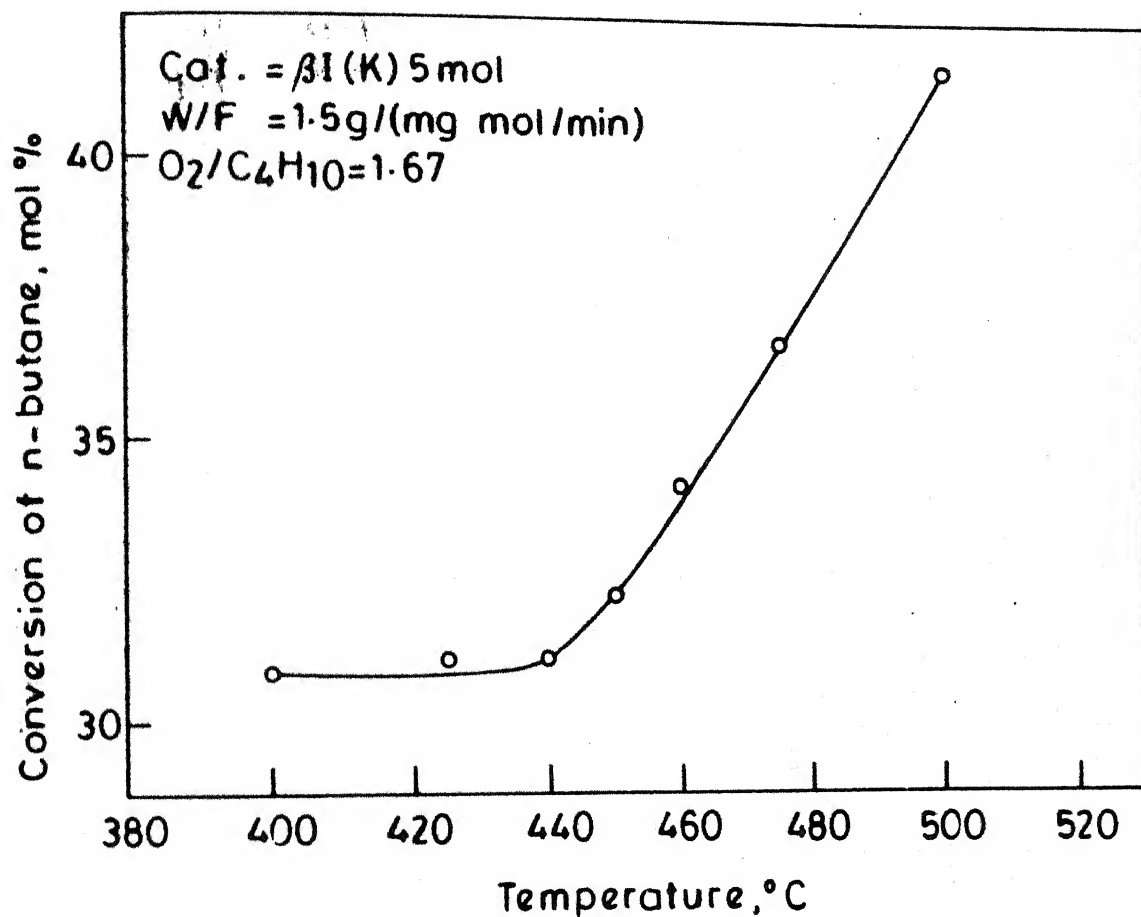
Fig. 5.15- Effect of temperature on conversion of n- butane.
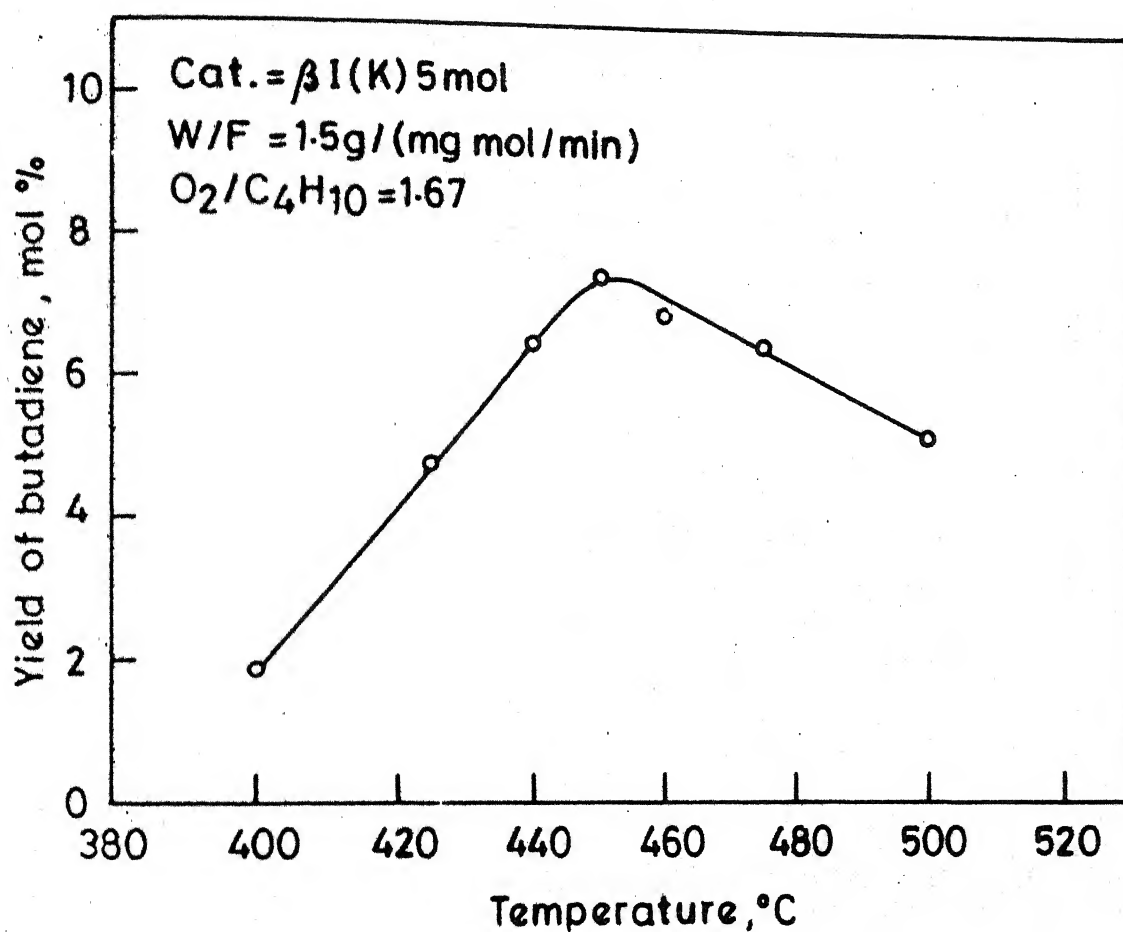
Fig. 5.16 – Effect of temperature on yield of butadiene.
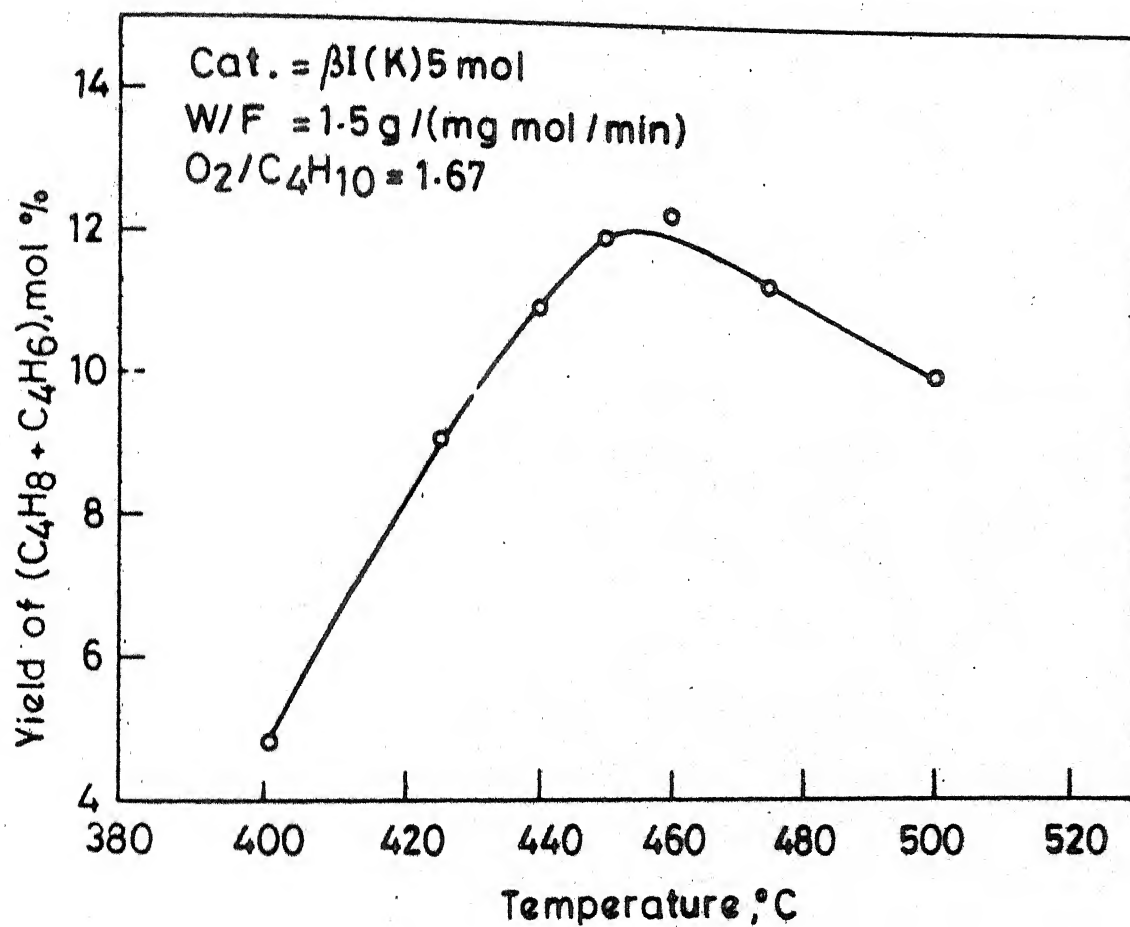
Fig. 5.17- Effect of temperature on yield of (butenes + butadiene).
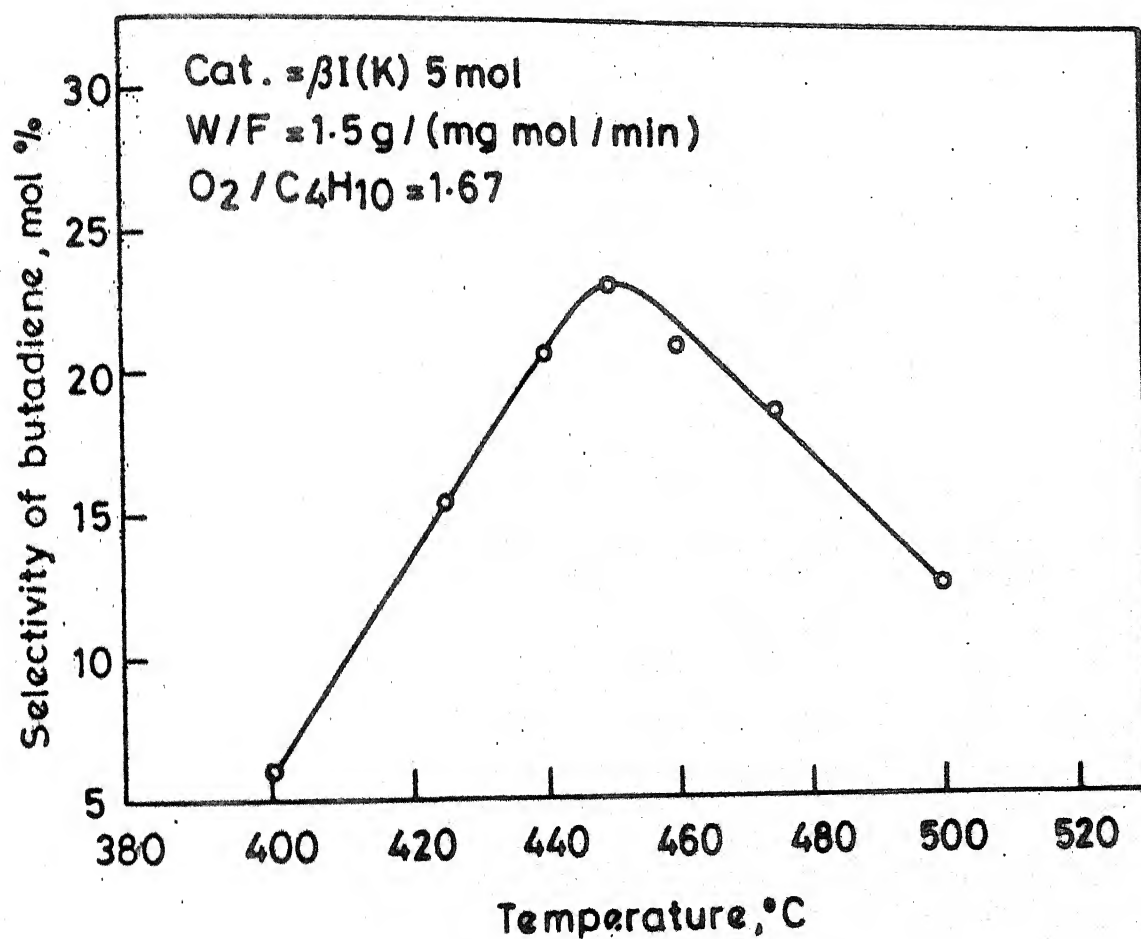
Fig. 5.18- Effect of temperature on selectivity of butadiene.
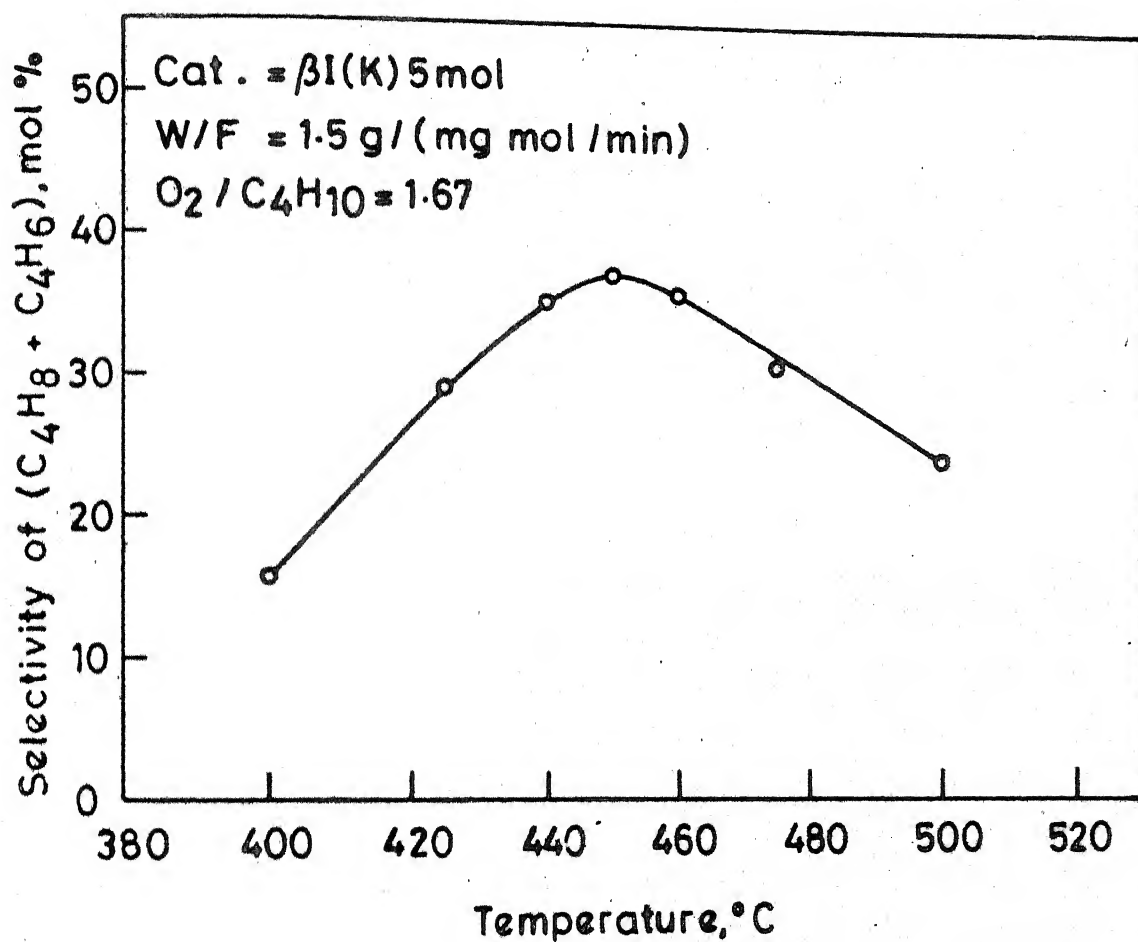
Fig. 5.19- Effect of temperature on selectivity of (butenes + butadiene).

selectivity is found to vary from about 15.8 mol% at 400°C to about 24.2 mol% at 500°C with a maximum of about 37.2 mol% at 450°C.

The overall behaviour with respect to the yield and selectivity of butadiene alone and combined with butenes is similar over the entire temperature range covered in this study. The optimum values are obtained at about 450°C. The yields and selectivities are lower at the temperatures higher than 450°C due to the formation of secondary products.

5.9 Effect of Oxygen to Butane Ratio on Conversion, Yield and Selectivity

The effect of oxygen to butane ratio is an important variable in the study of oxidative dehydrogenation reactions. Bismuth molybdate catalyst has a labile oxygen which may be released during the reaction. But it is likely to get deactivated faster due to excessive loss of its lattice oxygen at low oxygen concentrations in the gaseous feed. However, a lower limit of oxygen to butane ratio of 0.5 may be considered for an experimental study. The upper limit may be fixed at about 2.0 in view of the fact that butane air mixtures having oxygen to butane ratio between 2.25 and 10.9 are explosive [71]. The theoretical oxygen to butane ratio is 1.0. Further it is reported [10,21] that at oxygen to butane ratios greater than 11.0, complete oxygenated compounds dominate the product stream.

The experimental observations have been reported in Appendix III. The results have been summarised in Table 5.10. at specified conditions.

Fig. 5.20 shows the effect of oxygen to butane ratio on the conversion of n-butane. The conversion is found to increase with oxygen to butane ratio but it tends to reach a maximum at about an O_2/C_4H_{10} ratio of about 1.6. The increase in conversion with increasing oxygen availability is understandable. Oxygen is a reactant. It also reduces the effective partial pressure of butane. The dehydrogenation reactions are favoured at lower partial pressure of butane [72]. Further, the catalytic activity is improved at higher oxygen concentrations due to continuous removal of coke from the catalyst sites.

Figure 5.21 shows the effect of oxygen to butane ratio on yield of butadiene. The yield of butadiene is found to increase with O_2/C_4H_{10} ratio of about 1.5 and then it tends to level off. This observation is significant. In case of oxidative dehydrogenation of butenes to butadiene Welch et al. [69] found that the maximum yield of butadiene occurred at O_2/C_4H_8 ratio of 0.72. This ratio would work out to be 1.44 in the case of oxidative dehydrogenation of n-butane to butadiene which is in close agreement with the results of this study.

Fig. 5.22 shows the effect of oxygen to butane ratio on the combined yield of butenes and butadiene. The maximum

TABLE 5.10   EFFECT OF OXYGEN TO BUTANE RATIO ON CONVERSION,
             YIELD AND SELECTIVITY

Catalyst	: β I(K)
Catalyst weight	: 12.80 g
Active component	: $Bi_2O_3 \cdot 2MoO_3$
Catalyst concentration	: 5 mol/100 mol I(K)
Temperature	: 450°C
W/F	: 2.00 g/(mg mol/min)
Nitrogen to oxygen ratio	: 1.60

Oxygen/Butane \ Results	0.57	0.80	1.00	1.30	1.67
Conversion, mol%	13.70	20.07	25.76	30.29	32.15
Yield(bd), mol%	5.00	6.15	6.48	7.02	7.23
Yield (bute+ bd),mol%	7.57	8.50	9.48	10.89	12.05
Selectivity (bd), mol%	36.51	30.66	25.16	23.19	22.48
Selectivity (bute+bd), mol%	55.26	42.36	36.81	35.97	37.47
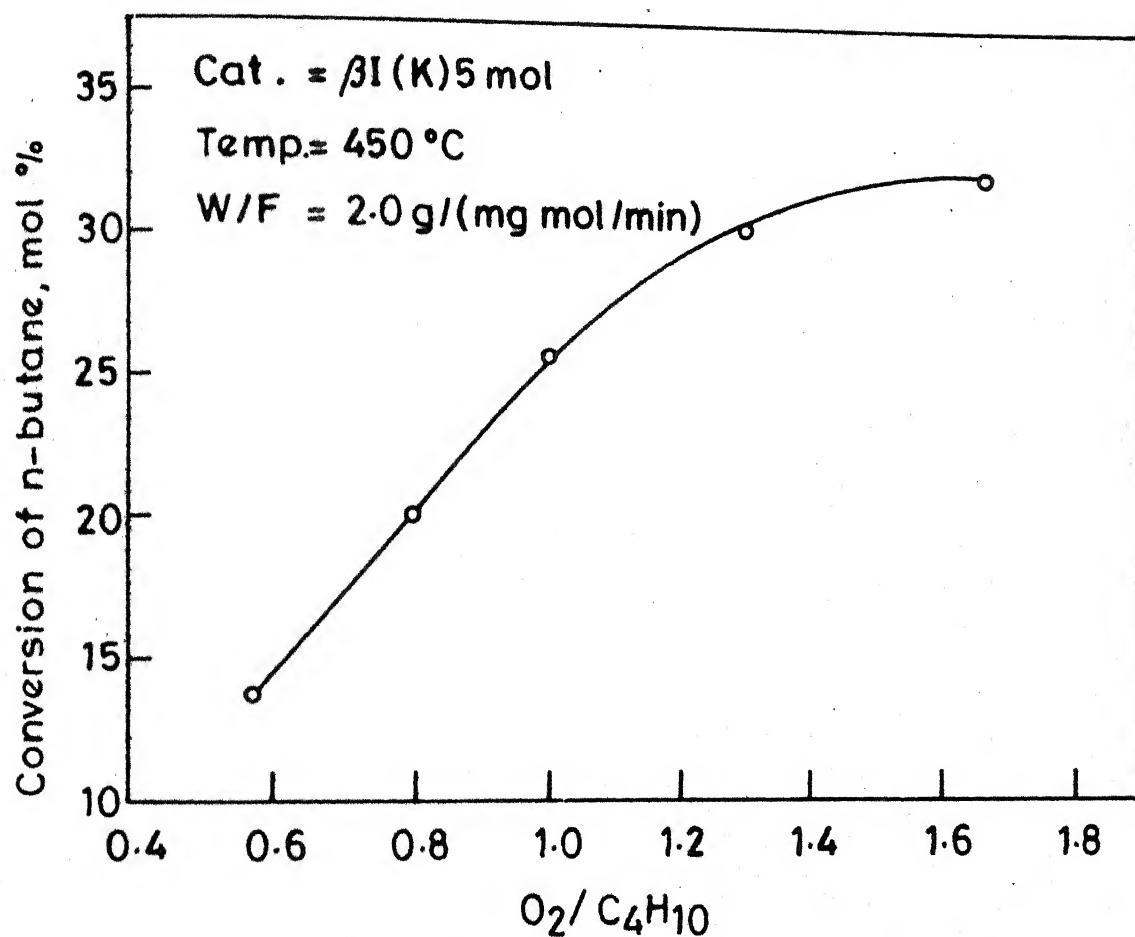
Fig. 5.20- Effect of oxygen to butane ratio on conversion
of n-butane.
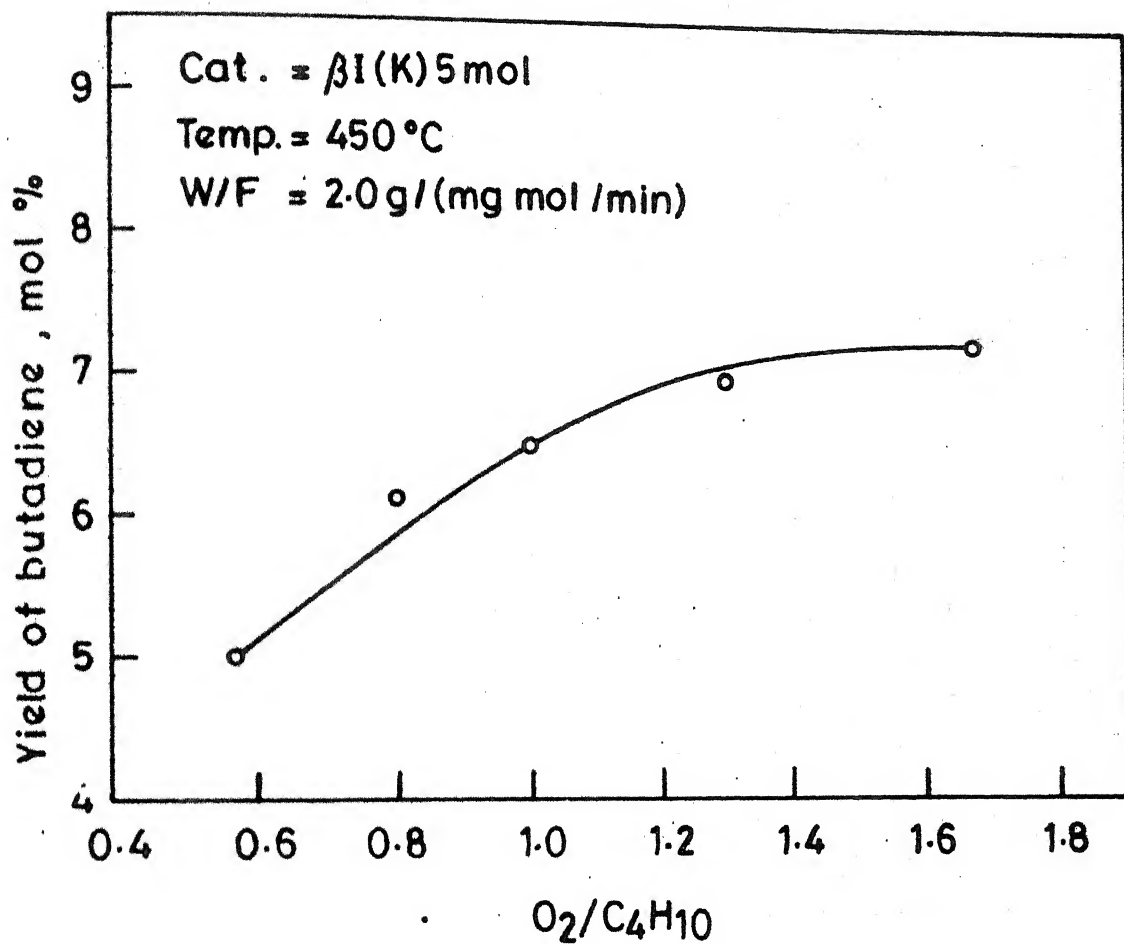
Fig.5·21– Effect of oxygen to butane ratio on yield of butadiene.
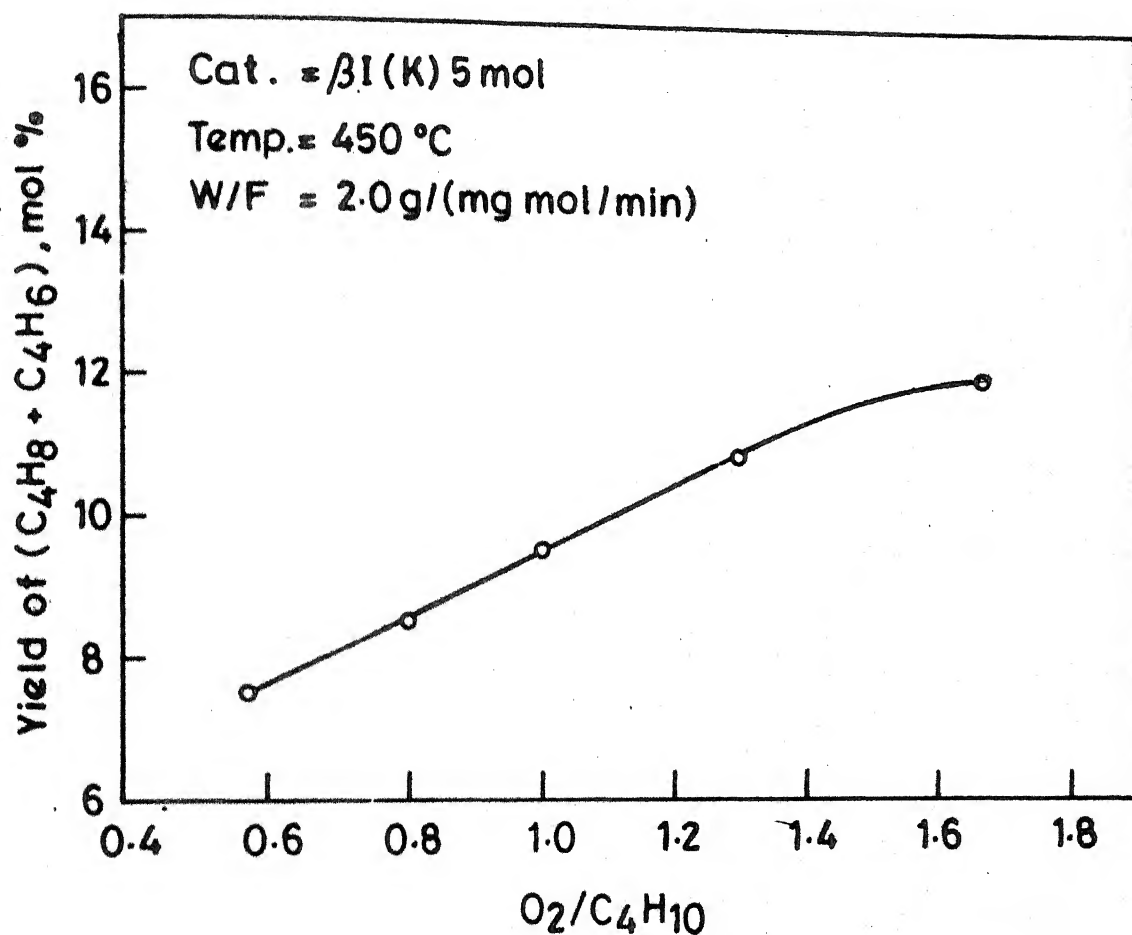
Fig. 5.22 – Effect of oxygen to butane ratio on yield of (butenes + butadiene).

per pass yield, about 12 mol%, was obtained at O_2/C_4H_{10} ratio of about 1.5.

Fig. 5.23 shows the effect of oxygen to butane ratio on the selectivity of butadiene. The selectivity is found to decrease from 36.5 mol% at 0.57 O_2/C_4H_{10} to about 23.0 mol% at oxygen to butane ratio of 1.30. Thereafter, it becomes almost constant.

Fig. 5.24 shows the effect of oxygen to butane ratio on the combined selectivity of butenes and butadiene. The selectivity is found to decrease from about 55.3 mol% to about 37 mol% as the oxygen to butane ratio is increased from 0.57 to about 1.0. Thereafter, it is found to remain almost constant. Similar behaviour has been reported by Welch et al. [69] for the butenes to butadiene system.

The optimum selectivity with respect to butadiene obtained with this catalyst is much higher at about 23 mol% as compared to about 9 mol% reported by Shenoy [15] . Hence, this catalyst seems to be more promising.

5.10 Kinetic Model for Oxidative Dehydrogenation of n-Butane

A kinetic model describing the behaviour of a catalytic reaction paves way to a better understanding of catalysis, improvements in catalyst design, accurate design of a chemical reactor and better insight in the behaviour of an existing reactor. In kinetic studies of heterogeneous catalytic reactions, the form
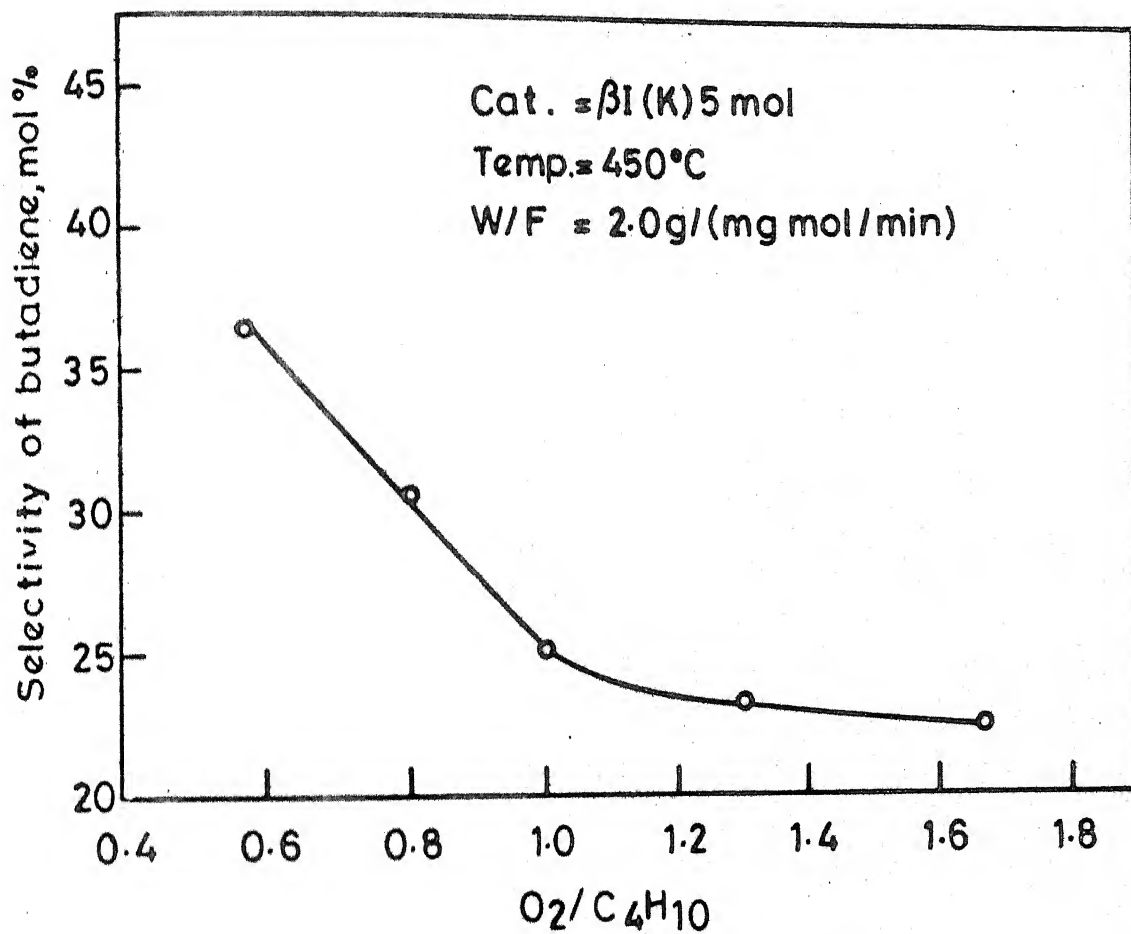
Fig. 5·23–Effect of oxygen to butane ratio on selectivity of butadiene.
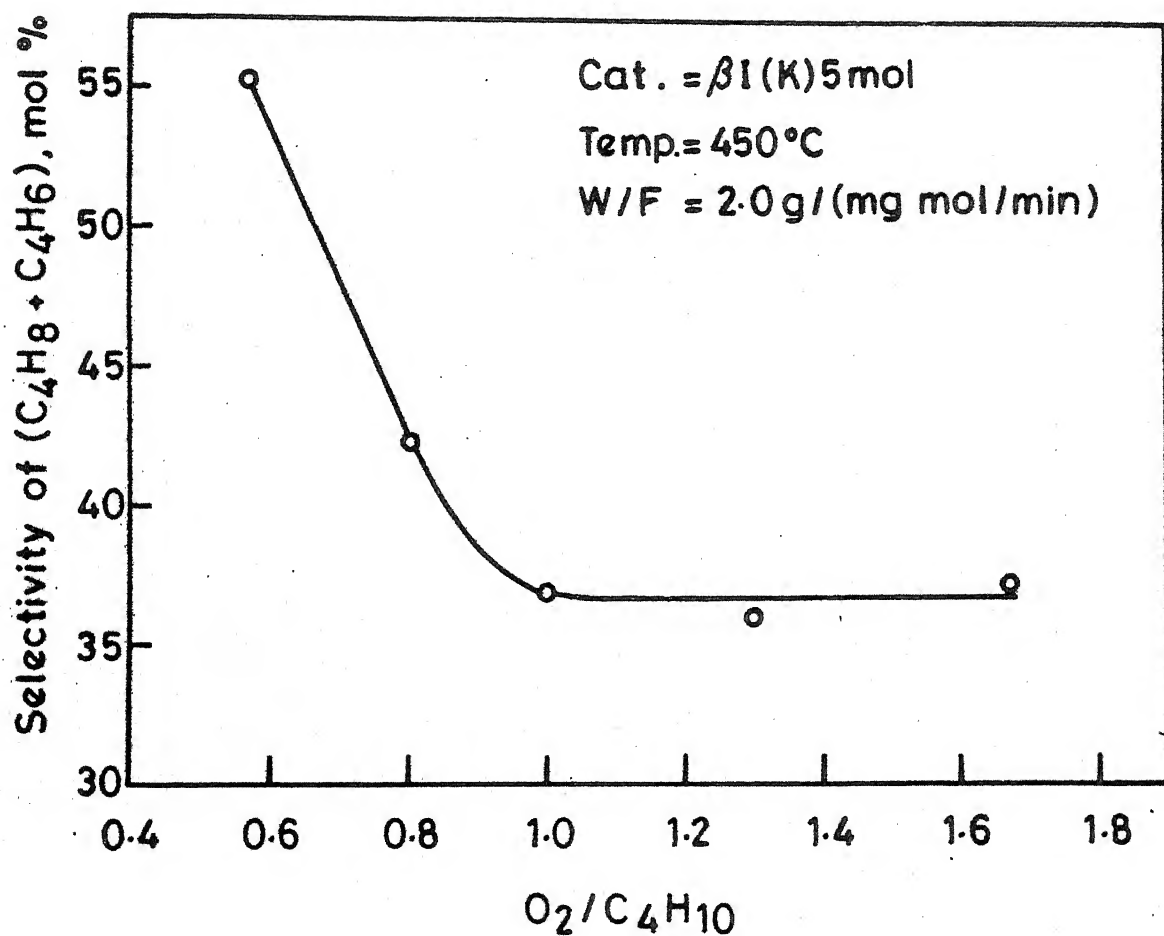
Fig. 5.24 - Effect of oxygen to butane ratio on selectivity of (butenes + butadiene).

of the model equation is seldom known beforehand. However,
physical-chemical laws governing adsorption and surface reactions
coupled with some formalism like, Hougen-Watson models, Langmuir-
Hinselwood models etc. may provide a narrow range of the forms
of model equations. To estimate the values of parameters in
model equations, experimental kinetic data, unmarked by external
mass transfer and pore diffusional resistances, are to be obtained
By increasing the flow rate of reactants, keeping W/F constant,
to a point beyond which no effect on product composition is
observed, one can assure that the external mass transfer resist-
ances are eliminated. Similarly, by decreasing the catalyst
particle size, pore diffusion resistances can be screened.
Several numerical methods are available for estimating the values
of parameters in the model. It is not uncommon that more than
one model fit the experimental data adequately, and at this
stage "model discrimination" can be applied to adjudge the
most plausible model. In addition, methods for reliability
analysis of the estimated parameters are also available. An
extensive review on this topic has been given by Froment and
Hosten [73] .

Kinetic data generated at low conversions can be analysed
by the means of a differential analysis. However, in complex
reactions, at low conversions the main products only are iden-
tified and a rigorous treatment of the data is not possible.
In such cases data at high conversions are obtained and integral

methods of analysis can be restored. In the following, a comprehensive model based on a single-site Hougen-Watson approach has been developed. Integral method of analysis was followed in analysing the experimental data. Failure to estimate the parameters has been explained.

Reaction Rate Model

Based on the Hougen-Watson approach, a single site mechanism which incorporates the features of redox mechanism, a kinetic model for the oxidative dehydrogenation of butane to butenes and butadiene may be represented by the following reaction scheme :

$$A \xrightarrow{F_1 k_1} B \xrightarrow{(1-F_3) k_2} D$$

with $A \xrightarrow{(1-F_1-F_2) k_1} D$, $A \xrightarrow{F_2 k_1} C$, $B \xrightarrow{F_3 k_2} C$, $C \xrightarrow{k_3} D$
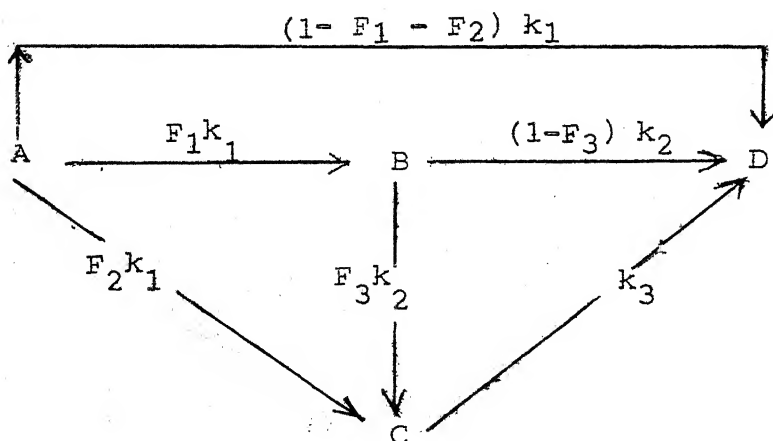
where

$$A \;=\; \text{Butane}$$

$$B \;=\; \text{Butenes}$$

$$C \;=\; \text{Butadiene}$$

$$D \;=\; CO, CO_2$$

and k_1, k_2 and k_3 are reaction rate constants. F_1 is the fraction

of butane producing butenes, F_2 is the fraction of butane produ-
cing butadiene and F_3 is the fraction of butenes producing buta-
diene, the rest goes to CO and CO_2.

The following steps are assumed :

$$O_2 + 1 \rightleftharpoons O_2 1 \tag{5.1}$$

$$O_2 1 + 1 \rightleftharpoons O1 + O1 \tag{5.2}$$

$$A + O1 \xrightarrow{k_1} B, C, D \tag{5.3}$$

$$A + 1 \rightleftharpoons A1 \tag{5.4}$$

$$B + 1 \rightleftharpoons B1 \tag{5.5}$$

$$C + 1 \rightleftharpoons C1 \tag{5.6}$$

$$B + O1 \xrightarrow{k_2} C, D \tag{5.7}$$

$$C + O1 \xrightarrow{k_3} D \tag{5.8}$$
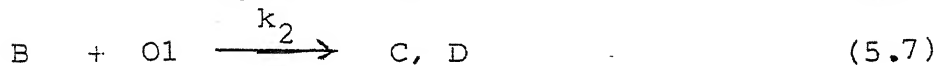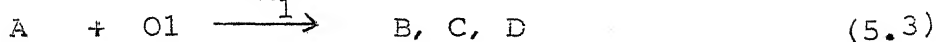
where

1 is denoted for vacant site and O1 is denoted for oxidised site.
In the above mechanism, steps (5.1),(5.2),(5.4),(5.5)&(5.6) are assumed
to be at equilibrium, while steps involving surface reactions (5.3),
(5.7), and (5.8) are assumed to be rate controlling. Only A, B, C
are assumed to be adsorbed on the vacant sites.

Corresponding equilibrium constants are

$$K_1 = \frac{C_{O_2 1}}{P_{O_2} \cdot C_1}$$

$$K_2 = \frac{C_{O1}^2}{C_{O_2 1} \cdot C_1}$$

$$K_4 = \frac{C_{A1}}{p_A \cdot C_1}$$

$$K_5 = \frac{C_{B1}}{p_B \cdot C_1}$$

$$K_6 = \frac{C_{C1}}{p_C \cdot C_1}$$

Where C denotes concentration and p denotes the partial pressure of gas.

From equation (3),

$$-r_A = k_1 p_A C_{O1} \qquad (5.9)$$

Using the site balance

$$C_t = C_1 + C_{O_2 1} + C_{O1} + C_{A1} + C_{B1} + C_{C1} \qquad (5.10)$$

r_A, r_B and r_C can be expressed as

$$(-r_A) = \frac{k_1' K_2' p_A p_{O_2}^{\frac{1}{2}}}{1 + K_1 p_{O_2} + K_2' p_{O_2}^{\frac{1}{2}} + K_4 p_A + K_5 p_B + K_6 p_C} \qquad (5.11)$$

in which $k_1' = K_1 C_t$ and $K_2' = \sqrt{K_1 K_2}$

$$(r_B) = (F_1 - \frac{k_2 p_B}{k_1 p_A}) \cdot (-r_A) \qquad (5.12)$$

and $\quad (r_C) = (F_2 + F_3 \cdot \dfrac{k_2 p_B}{k_1 p_A} - \dfrac{k_3 p_C}{k_1 p_A}) \cdot (-r_A)$ $\qquad$ (5.13)

In above differential equations (5.11), (5.12), (5.13), the number of parameters to be estimated are 11 which is large enough to cause severe convergence problem in the case of differential equation model if the rigorous multiresponse approach is followed. To circumvent this difficulty a possible approach has been discussed by Froment and Hosten [73] . According to this approach the yields of different products are considered as responses and preliminary estimates of ratios of rate constants are to be estimated. A schematic out line of this approach in the context of the present model is presented below.

The design equations for fixed bed reactors are given by

$$-r_A = \frac{dC_A}{dt} = \frac{dx}{dW/F_{A_O}} \qquad (5.14)$$

$$r_B = \frac{dC_B}{dt} = \frac{du}{dW/F_{A_O}} \qquad (5.15)$$

$$r_C = \frac{dC_C}{dt} = \frac{dv}{dW/F_{A_O}} \qquad (5.16)$$

where

$\quad x = $ conversion of A; and $p_A = p_{A_O}(1-x)$

$\quad u = $ conversion of A to B; and $p_B = u p_{A_O}$ $\qquad$ (5.17)

$\quad v = $ conversion of A to C; and $p_C = v p_{A_O}$

Dividing equations (5.15) and (5.16) by equation (5.14), substituting

values for r_B and r_C from equations (5.12) and (5.13) and expressing p_A, p_B, p_C in terms of conversion from relations (5.17), the above relations transform to

$$\frac{du}{dx} = F_1 - k_{21} \frac{u}{(1-x)} \tag{5.18}$$

and

$$\frac{dv}{dx} = F_2 + F_3 k_{21}\frac{u}{(1-x)} - k_{31} \frac{v}{(1-x)} \tag{5.19}$$

in which

$$k_{21} = k_2/k_1$$

$$k_{31} = k_3/k_1$$

The solutions of equations (5.18) and (5.19) are given by

$$u = \frac{F_1}{1-k_{21}} \left\{ (1-x)^{k_{21}} - (1-x) \right\} \tag{5.20}$$

and

$$v = \frac{F_2}{1-k_{31}} \left\{ (1-x)^{k_{31}} - (1-x) \right\} +$$

$$\frac{F_1 \cdot F_3 \cdot k_{21}}{1-k_{21}} \left[\frac{1}{k_{21}-k_{31}} \left\{ (1-x)^{k_{31}} - (1-x)^{k_{21}} \right\} \right.$$

$$\left. - \frac{1}{1-k_{31}} \left\{ (1-x)^{k_{31}} - (1-x) \right\} \right] \tag{5.21}$$

Parameter Estimation

In the equations (5.20) and (5.21) u represents the yield of butenes and v represents the yield of butadiene. Since these parameters were measured for all the experiments, it is possible to estimate F_1, k_{21}, F_2, F_3 and k_{31} from the relevent algebric model equations (5.20) and (5.21), The other six parameters in the differential equation model (5.11) can now be estimated treating it as a single response model.

The experimental data for the present system demonstrate that the responses are highly insensitive to space velocity (W/F) changes, in which case numerical integration of equation (5.11) does not make sense and at this stage the efforts toward the conventional approach for kinetic modelling was abandoned.

A comprehensive model based on Hougen-Watson approach, a single site mechanism which incorporates the features of redox mechanism, was examined. Since the experimental data are highly insensitive to the space velocity for the responses (conversion and yield), the values of parameters in the developed model could not be estimated. The insensitivity of the response with the space velocity as observed in this study is not a new finding. It has been noted in several selective oxidation reactions [69,74] The possible explanation for it may be, as some authors [75] have pointed out, that chain reaction is initiated at the surface of catalyst and propogates in the gas phase thus eliminating all mass transfer factors.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The main aim of the present work was to develop a suitable catalyst for the single step oxidative dehydrogenation process of n-butane to butadiene. Accordingly, bismuth molybdate catalysts incorporating iron oxide supported on alumina were developed. X-ray and electron microscopic studies confirmed that the bismuth molybdate catalysts were in their pure β - and γ -phases and chemical interactions among different constituents were absent. Thermal stability studies of the catalysts carried out by calcination of both β - and γ - phases of pure as well as supported catalysts upto 600°C did not show any structural changes.

The detailed experimental investigations *of three different catalysts of various concentrations* indicated β - bismuth molybdate with 5 mol per 100 mol I(K) catalyst concentration to be the best catalyst. The effect of space velocity on conversion, yield and selectivity was found to be insignificant over the temperature range and the oxygen to butane ratios studied in this work. The maximum yield and selectivity of butadiene were obtained at the temperature of 450°C and at oxygen to butane ratio of about 1.5. A per pass yield of 7.25 mol % and a selectivity of 23 mol % with respect to butadiene were obtained. The combined yield of (butenes + butadiene) was 12 mol % and the combined selectivity was 37 mol % under the optimum conditions.

Hence β -bismuth molybdate with 5 mol per 100 mol I(K) catalyst concentration appears to be highly promising for this

industrially important reaction.

Recommendations for the Future Work

1. The single step oxidative dehydrogenation of n-butane to
    butadiene may be studied by using a catalyst of low surface
    area. With such a catalyst, the space velocity (W/F)
    variations are likely to provide more meaningful informa-
    tions for the kinetic modelling.

2. The effect of addition of steam to the feed may be studied.
    In addition to serve as a heat sink and as a diluent to
    achieve the desired low pressure benefits, steam is likely
    to suppress the side reactions also.

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APPENDICES

APPENDIX I

CHEMICAL ANALYSIS OF CATALYSTS

The chemical analysis of the catalyst was done by the atomic absorption spectrometry. This technique makes use of the fact that neutral or ground state atoms of an element can absorb electromagnetic radiation over a series of very narrow and sharply defined wavelengths. The sample, in solution, is aspirated as a fine mist into a flame where it is converted to an atomic vapour. Most of the atoms remain in the ground state and are, therefore, capable of absorbing radiation of a suitable wavelength. This discrete radiation is usually supplied by a hollow cathode lamp which is a sharp line source consisting of a cathode containing the element to be determined along with a tungusten anode.

When a sufficient voltage is applied across the electrodes, the filler gas is ionized and the ions are accelerated towards the cathode. As these ions bombard the cathode, they cause the cathode material to "sputter" and form an atomic vapour in which atoms exist in an excited electronic state. In returning to the ground state, the line characteristics of the element are emitted and pass through the flame where they may be absorbed by the atomic vapour. Generally, only the test element can absorb this radiation. Therefore, this method becomes very

specific in addition to being quite sensitive.

In atomic emission spectroscopy the metal is excited from the energy imparted to it thermally by the flame and then as it returns to the ground state it emits radiation at a characteristic wavelength. This radiation is then isolated by a monochromator and subsequently its intensity is directly proportional to the concentration of the element present.

Preparation of the Standard Solution

1.0 g of metallic bismuth was dissolved in a minimum volume of 1:1 nitric acid. It was then diluted quantitatively to a volume of 1:1 with 2% (V/V) nitric acid to obtain a final concentration of 1000 μg/ml bismuth.

Analysis Method

The standard solution was prepared as discussed above. The solution was further diluted and five samples were prepared within the linear range of 1-15 μg/ml of bismuth concentration. A calibration plot was then constructed as bismuth concentration versus intensity of radiation.

The solution of the test sample (catalyst) was made using the same solvent. It was then diluted within the same linear range to get four to five sample solutions. These samples solutions were used to get different intensities of radiation which, with the help of calibration plot, gave the corresponding

concentrations of bismuth, in the solution. Since the dilution of the test sample was known, the concentration of bismuth in the test sample could be estimated.

Similarly the concentrations of molybdenum in catalyst samples were determined.

Appendix II

MODEL CALCULATIONS

Run Number 1

Weight of catalyst, W = 12.80 g

Corresponding to a desired W/F ratio of 2.50 g/(mg mol/min), the total inlet gas flow rate, F = 12.80/2.50

$$= 5.12 \text{ mg/mol/min}$$

Using standard conditions, 1 cm^3 of gas at room temperature ($\sim$ 25°C) and atmospheric pressure corresponds to 0.0409 mg mol.

$$\text{Hence} \quad F = \frac{5.12}{0.0409} \quad cm^3/min$$

$$= 125.18 \; cm^3/min$$

The total inlet gas flow rate can be related to the individual gas flow rates by the relation :

$$F_{butane} + F_{oxygen} + F_{nitrogen} = F \qquad (1)$$

Therefore,

$$\frac{F_{butane}}{F_{oxygen}} + \frac{F_{oxygen}}{F_{oxygen}} + \frac{F_{nitrogen}}{F_{oxygen}} = \frac{F}{F_{oxygen}} \qquad (2)$$

Corresponding to the ratios of F_{butane}/F_{oxygen} of 0.6 and $F_{nitrogen}/F_{oxygen}$ of 1.6, Equation (2) can be written as

$$0.6 + 1 + 1.6 = \frac{125.18}{F_{oxygen}} \qquad (3)$$

or

$$F_{oxygen} = 39.12 \ cm^3/min$$

From which

$$F_{butane} = 39.12 \times 0.6 = 23.47 \ cm^3/min$$

$$F_{nitrogen} = 39.12 \times 1.6 = 62.59 \ cm^3/min$$

Total F = 125.18 cm^3/min

Based on the above flow rates, the feed gas composition is given by

Butane (23.47/125.18) 100 = 18.72%

Oxygen (39.12/125.18) 100 = 31.26%

Nitrogen (62.59/125.18) 100 = 50.02%

Dry exit gas analysis (By gas chromatographic and Orsat analysis)

Products	Composition, mol%
Ethylene	0.00
Propylene	0.00
n-Butane	14.04
n-Butene	0.24
trans-2-Butene	0.32
cis-2-Butene	0.32
1,3-Butadiene	1.36
Methane	0.00
Carbon dioxide	14.66
Oxygen	10.03
Carbon monoxide	3.47
Nitrogen	55.58

Since nitrogen is an inert gas, a tie balance for nitrogen was made.

Molar feed rate of nitrogen = 5.12 x 0.5002

= 2.56 mg mol/min

Molar flow rate of nitrogen is product gas

= 4.61 x .5558

= 2.56 mg mol/min

Hence, for a feed rate of 5.12 mg mol/min the dry exit gas flow rate corrosponds to 4.61 mg mol/min.

Calculations for Results

Molar feed rate of butane = 5.12 x 0.1872 mg mol/min

= 0.9585 mg mol/min

Molar flow rate of butane in product

= 4.61 x 0.1404 mg mol/min

= 0.6472 mg mol/min

mol of butane converted = 0.9585 - 0.6472

= 0.3113

mol of net (butenes + butadiene) formed

= (0.0024 + 0.3032 + 0.0032 +0.0136)4.61

= 0.1033 mg mol/min

mol of net butadiene formed

= 0.0136 x 4.61 mg mol/min

= 0.0627 mg mol/min

Conversion, mol % $\quad = \dfrac{0.3113}{0.9585}$ x 100 $\quad = \quad$ 32.51

Yield of butadiene, mol %

$$= \dfrac{0.0627}{0.9585} \text{ x } 100 \quad = \quad 6.52$$

Yield of (butenes + butadiene), mol%

$$= \dfrac{0.1033}{0.9585} \text{ x } 100 \quad = \quad 10.73$$

Selectivity of butadiene, mol %

$$= \dfrac{0.0627}{0.3113} \text{ x } 100 \quad = \quad 20.04$$

Selectivity of (butenes + butadiene), mol%

$$= \dfrac{0.1033}{0.3113} \text{ x } 100 = \quad 32.99$$

Appendix III

EXPERIMENTAL RESULTS

RUN NO	1	2	3	4	5
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	5.12	5.12	5.12	5.12	5.12
W/F,G/(MG MOL/MIN)	2.50	2.50	2.50	2.50	2.50
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.00	0.11	0.11	0.00	0.00
PROPELENE,%	0.00	0.00	0.00	0.00	0.00
N-BUTANE,%	14.04	14.04	15.08	14.58	14.02
N-BUTENE,%	0.24	0.26	0.22	0.22	0.21
TRANCE-2-BUTENE,%	0.32	0.31	0.32	0.29	0.31
CIS-2-BUTENE,%	0.32	0.32	0.32	0.35	0.32
1,3-BUTADIENE,%	1.36	1.44	1.27	1.40	1.50
METHANE,%	0.00	0.00	0.00	0.00	0.00
CARBON DIOXIDE,%	14.66	16.27	15.06	14.25	15.52
OXYGEN,%	10.03	10.49	12.04	11.78	10.33
CARBON MONOXIDE,%	3.47	1.47	0.00	1.53	2.21
NITROGEN,%	55.58	55.58	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	4.61	4.61	4.61	4.61	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	32.51	32.60	27.51	29.89	32.60
YIELD BD,%	6.52	6.94	6.09	5.74	7.21
YIELD BUTE(S)+BD,%	10.73	11.27	10.25	10.91	11.28
SELECT BD,%	20.04	21.35	22.14	22.55	22.12
SELECT BUTE(S)+BD,%	32.99	34.66	37.27	36.50	34.62

INLET CONDITIONS AND SET POINTS

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RUN NO	6	7	8	9	10
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	3.00	3.00	3.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	32.47	18.72	18.72	18.72
OXYGEN CONC,%	25.97	25.97	31.26	31.26	31.26
NITRON CONC,%	41.56	41.55	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	25.60	25.60	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	0.50	0.50	2.50	2.00	1.75
OXYGEN:BUTANE	0.80	0.80	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.50	1.60	1.50

OUTLET CONCENTRATIONS

	6	7	8	9	10
ETHYLENE,%	0.91	0.85	0.29	0.00	0.29
PROPELENE,%	0.32	0.23	0.00	0.00	0.00
N-BUTANE,%	28.13	27.34	14.32	14.63	14.83
N-BUTENE,%	0.42	0.41	0.00	0.25	0.21
TRANCE-2-BUTENE,%	0.42	0.41	0.50	0.37	0.44
CIS-2-BUTENE,%	0.38	0.41	0.50	0.25	0.29
1,3-BUTADIENE,%	1.72	1.90	1.02	1.09	1.10
METHANE,%	2.33	2.06	0.00	0.00	0.47
CARBON DIOXIDE,%	11.99	13.65	15.01	14.81	14.08
OXYGEN,%	4.30	2.30	10.52	10.98	12.10
CARBON MONOXIDE,%	2.89	4.24	2.26	2.04	0.63
NITROGEN,%	46.18	46.48	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	23.04	23.04	4.61	5.76	6.58

CONVERSION,YIELD,SELECTIVITY

	6	7	8	9	10
CONVERSION,%	22.03	24.20	31.17	29.58	28.72
YIELD BD,%	4.76	5.27	4.90	5.26	5.28
YIELD BUTE(S)+BD,%	8.17	8.72	9.71	9.42	9.79
SELECT BD,%	21.63	21.75	15.72	17.72	18.39
SELECT BUTE(S)+BD,%	37.11	36.01	31.14	31.75	34.09

INLET CONDITIONS AND SET POINTS

RUN NO	11	12	13	14	15
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	3.00	3.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.60	1.68	0.00	0.00	0.40
PROPELENE,%	0.30	0.69	0.00	0.00	0.00
N-BUTANE,%	14.36	15.45	14.04	14.11	14.53
N-BUTENE,%	0.30	0.25	0.24	0.28	0.25
TRANCE-2-BUTENE,%	0.30	0.37	0.32	0.40	0.32
CIS-2-BUTENE,%	0.30	0.25	0.32	0.32	0.32
1,3-BUTADIENE,%	1.12	0.98	1.36	1.60	1.48
METHANE,%	0.65	0.88	0.00	0.00	0.50
CARBON DIOXIDE,%	14.63	14.05	14.66	14.93	14.50
OXYGEN,%	11.59	9.02	10.03	11.08	12.13
CARBON MONOXIDE,%	0.27	0.00	3.47	1.79	0.00
NITROGEN,%	55.58	55.68	55.58	55.68	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	30.95	25.71	32.51	32.45	30.15
YIELD BD,%	5.39	4.72	6.52	7.23	7.11
YIELD BUTE(S)+BD,%	9.73	8.90	10.73	12.05	11.36
SELECT BD,%	17.43	18.37	20.04	22.48	23.59
SELECT BUTE(S)+BD,%	31.45	34.61	32.99	37.47	37.69

INLET CONDITIONS AND SET POINTS

RUN NO	16	17	18	19	20
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	7.00	7.00	7.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.30	0.22	0.00	0.22	1.05
PROPELENE,%	0.00	0.36	0.00	0.00	0.31
N-BUTANE,%	14.09	14.73	14.57	14.48	14.87
N-BUTENE,%	0.31	0.29	0.00	0.00	0.21
TRANCE-2-BUTENE,%	0.31	0.29	0.32	0.42	0.29
CIS-2-BUTENE,%	0.31	0.29	0.32	0.42	0.42
1,3-BUTADIENE,%	1.56	1.46	1.31	1.45	1.31
METHANE,%	0.59	3.63	0.00	0.00	0.00
CARBON DIOXIDE,%	12.84	12.04	14.37	14.25	14.81
OXYGEN,%	11.28	11.21	11.10	11.76	11.15
CARBON MONOXIDE,%	2.82	0.00	2.33	1.42	0.00
NITROGEN,%	55.58	55.58	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.76	6.58

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	32.25	29.20	29.46	30.38	28.53
YIELD BD,%	7.48	7.02	6.31	6.95	6.30
YIELD BUTE(S)+BD,%	12.00	11.03	9.39	11.02	10.70
SELECT BD,%	23.19	24.05	21.41	22.93	22.07
SELECT BUTE(S)+BD,%	37.21	38.47	31.87	35.26	37.52

INLET CONDITIONS AND SET POINTS

RUN NO	21	22	23	24	25
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	7.00	7.00	9.00	9.00	9.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
TN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	21	22	23	24	25
ETHYLENE,%	0.42	0.76	0.27	0.62	0.93
PROPELENE,%	0.44	0.62	0.00	0.00	0.32
N-BUTANE,%	14.73	14.92	14.84	14.92	14.98
N-BUTENE,%	0.25	0.22	0.00	0.25	0.21
TRANCE-2-BUTENE,%	0.30	0.29	0.37	0.26	0.25
CIS-2-BUTENE,%	0.25	0.29	0.00	0.26	0.25
1,3-BUTADIENE,%	1.45	1.36	1.25	1.25	1.17
METHANE,%	0.87	1.15	0.00	0.00	0.52
CARBON DIOXIDE,%	14.10	15.31	14.89	15.51	15.27
OXYGEN,%	11.62	9.58	10.89	11.33	10.53
CARBON MONOXIDE,%	0.00	0.00	1.91	0.00	0.00
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

	21	22	23	24	25
CONVERSION,%	29.16	28.27	28.63	28.26	27.98
YIELD BD,%	6.97	6.55	6.00	6.00	5.62
YIELD BUTE(S)+BD,%	10.81	10.44	7.78	9.75	9.04
SELECT BD,%	23.90	23.22	20.94	21.24	20.09
SELECT BUTE(S)+BD,%	37.08	36.94	27.49	34.51	32.33

RUN NO	26	27	28	29	30
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	GAMMA	GAMMA	GAMMA
CAT CONC,MOL/100 MOL	9.00	9.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITROGEN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	6.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	26	27	28	29	30
ETHYLENE,%	0.88	1.68	0.00	0.00	0.00
PROPELENE,%	0.40	0.49	0.00	0.00	0.00
N-BUTANE,%	15.14	15.19	14.88	14.53	14.49
N-BUTENE,%	0.23	0.23	0.00	0.21	0.25
TRANCE-2-BUTENE,%	0.35	0.23	0.38	0.27	0.24
CIS-2-BUTENE,%	0.23	0.23	0.38	0.30	0.30
1,3-BUTADIENE,%	1.17	1.22	0.70	0.72	0.71
METHANE,%	0.46	1.19	0.00	0.00	0.00
CARBON DIOXIDE,%	14.93	14.65	15.51	14.73	14.95
OXYGEN,%	10.63	9.42	10.27	9.32	9.17
CARBON MONOXIDE,%	0.00	0.00	2.30	4.34	4.31
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.76	6.58

CONVERSION,YIELD,SELECTIVITY

	26	27	28	29	30
CONVERSION,%	27.23	26.07	28.47	30.12	30.35
YIELD BD,%	5.61	5.88	3.38	3.46	3.40
YIELD BUTE(S)+BD,%	9.49	9.22	7.06	7.20	7.20
SELECT BD,%	20.59	21.79	11.88	11.47	11.21
SELECT BUTE(S)+BD,%	34.85	34.16	24.81	23.89	23.71

RUN NO	31	32	33	34	35
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	GAMMA	GAMMA	GAMMA	GAMMA	GAMMA
CAT CONC,MOL/100 MOL	5.00	5.00	10.00	10.00	10.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.57	1.57	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	31	32	33	34	35
ETHYLENE,%	0.26	0.26	0.00	0.89	0.00
PROPELENE,%	0.00	0.32	0.00	0.00	0.00
N-BUTANE,%	14.39	14.74	13.48	13.70	13.70
N-BUTENE,%	0.21	0.25	0.00	0.29	0.20
TRANCE-2-BUTENE,%	0.29	0.25	0.30	0.24	0.22
CIS-2-BUTENE,%	0.21	0.25	0.30	0.28	0.33
1,3-BUTADIENE,%	0.69	0.72	0.98	1.08	1.13
METHANE,%	0.87	1.40	0.00	0.00	1.17
CARBON DIOXIDE,%	14.64	14.64	14.46	14.62	14.42
OXYGEN,%	8.87	10.78	6.36	8.89	7.96
CARBON MONOXIDE,%	3.98	1.40	8.56	5.43	5.30
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.76	6.58

CONVERSION,YIELD,SELECTIVITY

	31	32	33	34	35
CONVERSION,%	30.80	29.13	35.21	34.14	34.14
YIELD BD,%	3.33	3.47	4.70	5.21	5.44
YIELD BUTE(S)+BD,%	6.74	7.11	7.55	9.10	9.03
SELECT BD,%	10.81	11.92	13.35	15.25	15.93
SELECT BUTE(S)+BD,%	21.88	24.89	21.44	25.66	26.44

INLET CONDITIONS AND SET POINTS

RUN NO	35	37	38	39	40
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	GAMMA	GAMMA	GAMMA	GAMMA	GAMMA
CAT CONC,MOL/100 MOL	10.00	10.00	15.00	15.00	15.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.41	0.63	0.00	0.00	0.00
PROPELENE,%	0.32	0.45	0.00	0.00	0.00
N-BUTANE,%	13.24	13.63	13.65	13.50	13.43
N-BUTENE,%	0.24	0.22	0.19	0.25	0.00
TRANCE-2-BUTENE,%	0.24	0.30	0.37	0.25	0.38
CIS-2-BUTENE,%	0.24	0.30	0.28	0.34	0.38
1,3-BUTADIENE,%	1.09	1.08	1.21	1.22	1.28
METHANE,%	0.90	1.59	0.00	0.00	0.81
CARBON DIOXIDE,%	15.25	14.81	14.53	14.26	13.87
OXYGEN,%	7.47	9.27	8.33	7.91	7.64
CARBON MONOXIDE,%	5.02	2.23	5.87	5.69	6.63
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	36.35	34.48	34.35	35.10	35.44
YIELD BD,%	5.24	5.19	5.81	5.88	6.16
YIELD BUTE(S)+BD,%	8.78	9.18	9.84	9.93	9.83
SELECT BD,%	14.43	15.06	16.91	15.76	17.38
SELECT BUTE(S)+BD,%	24.14	26.62	28.64	28.28	27.73

INLET CONDITIONS AND SET POINTS

RUN NO	41	42	43	44	45
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	GAMMA	GAMMA	GAMMA	GAMMA	GAMMA
CAT CONC,MOL/100 MOL	15.00	15.00	20.00	20.00	20.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	41	42	43	44	45
ETHYLENE,%	0.00	0.63	0.00	0.00	0.00
PROPELENE,%	0.00	0.62	0.00	0.00	0.00
N-BUTANE,%	13.34	13.47	15.26	13.83	14.07
N-BUTENE,%	0.42	0.25	0.25	0.25	0.25
TRANCE-2-BUTENE,%	0.33	0.32	0.36	0.25	0.32
CIS-2-BUTENE,%	0.33	0.32	0.36	0.32	0.22
1,3-BUTADIENE,%	1.12	1.20	1.12	1.15	1.20
METHANE,%	0.80	0.99	0.00	0.00	0.80
CARBON DIOXIDE,%	14.28	15.43	15.52	14.92	14.49
OXYGEN,%	7.88	9.62	11.57	8.62	9.37
CARBON MONOXIDE,%	5.92	1.80	0.00	5.08	3.71
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.76	6.58

CONVERSION,YIELD,SELECTIVITY

	41	42	43	44	45
CONVERSION,%	35.85	35.26	26.65	33.49	32.37
YIELD BD,%	5.40	5.75	5.39	5.63	5.75
YIELD BUTE(S)+BD,%	10.62	9.99	10.01	9.45	9.53
SELECT BD,%	15.07	16.30	20.24	15.51	17.75
SELECT BUTE(S)+BD,%	29.61	28.03	37.57	28.21	29.44

RUN NO	46	47	48	49	50
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	GAMMA	GAMMA	BI2/O3	BI2/O3	BI2/O3
CAT CONC,MOL/100 MOL	20.00	1.60	1.50	1.50	1.50
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRSN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	6.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	46	47	48	49	50
ETHYLENE,%	0.31	0.47	0.00	0.00	0.00
PROPELENE,%	0.00	0.54	0.00	0.00	0.00
N-BUTANE,%	13.65	13.84	15.32	15.55	15.50
N-BUTENE,%	0.36	0.22	0.00	0.00	0.28
TRANCE-2-BUTENE,%	0.48	0.32	0.51	0.45	0.28
CIS-2-BUTENE,%	0.00	0.32	0.51	0.49	0.28
1,3-BUTADIENE,%	1.22	1.47	0.73	0.75	0.78
METHANE,%	0.87	1.42	0.00	0.00	0.00
CARBON DIOXIDE,%	14.36	13.47	14.45	13.68	13.76
OXYGEN,%	8.68	10.39	12.43	12.92	12.54
CARBON MONOXIDE,%	4.50	2.27	0.47	0.59	1.02
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

	46	47	48	49	50
CONVERSION,%	34.36	33.46	26.34	25.26	25.50
YIELD BD,%	5.86	5.62	3.49	3.60	3.75
YIELD BUTE(S)+BD,%	9.91	9.77	8.40	8.11	7.73
SELECT BD,%	17.06	16.78	13.26	14.26	14.72
SELECT BUTE(S)+BD,%	28.85	29.19	31.90	32.10	30.33

INLET CONDITIONS AND SET POINTS

RUN NO	51	52	53	54	55
TEMP,*C	450.00	450.00	400.00	400.00	400.00
ACTIVE COMPONENT	BI2/O3	BI2/O3	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	1.50	1.60	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	40.25	40.25	40.25
OXYGEN CONC,%	31.26	31.26	22.98	22.98	22.98
NITRGN CONC,%	50.02	50.02	36.77	35.77	36.77
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.59	6.40
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.25	2.00
OXYGEN:BUTANE	1.67	1.67	0.57	0.57	0.57
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	51	52	53	54	55
ETHYLENE,%	0.00	0.00	0.00	0.00	0.00
PROPELENE,%	0.00	0.00	0.00	0.00	0.24
N-BUTANE,%	15.15	15.70	39.47	39.31	39.28
N-BUTENE,%	0.31	0.21	0.31	0.21	0.00
TRANCE-2-BUTENE,%	0.31	0.38	0.36	0.22	0.37
CIS-2-BUTENE,%	0.31	0.38	0.36	0.56	0.59
1,3-BUTADIENE,%	0.71	0.72	0.86	0.75	0.84
METHANE,%	0.00	0.00	0.00	0.00	0.75
CARBON DIOXIDE,%	14.74	13.87	7.99	7.62	7.95
OXYGEN,%	11.62	13.89	4.35	3.43	4.01
CARBON MONOXIDE,%	1.26	0.27	5.45	7.14	5.10
NITROGEN,%	55.58	55.68	40.86	40.86	40.86
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.12	5.76

CONVERSION,YIELD,SELECTIVITY

	51	52	53	54	55
CONVERSION,%	27.18	24.63	11.73	12.10	12.17
YIELD BD,%	3.42	3.46	1.93	1.68	1.88
YIELD BUTE(S)+BD,%	7.95	8.43	4.22	3.90	4.04
SELECT BD,%	12.59	14.09	16.45	13.90	15.48
SELECT BUTE(S)+BD,%	29.24	33.44	35.98	32.26	33.18

INLET CONDITIONS AND SET POINTS

RUN NO	55	57	58	59	60
TEMP,*C	400.00	400.00	400.00	400.00	400.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	40.25	40.25	32.47	32.47	32.47
OXYGEN CONC,%	22.98	22.98	25.97	25.97	25.97
NITRGN CONC,%	36.77	36.77	41.56	41.56	41.56
IN FLOW,MG MOL/MIN	7.31	8.63	5.12	5.69	6.40
W/F,G/(MG MOL/MIN)	1.75	1.50	2.50	2.25	2.00
OXYGEN:BUTANE	0.57	0.57	0.80	0.80	0.80
NITROGEN:OXYGEN	1.60	1.60	1.50	1.50	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.21	0.48	0.00	0.00	0.42
PROPELENE,%	0.30	0.60	0.00	0.00	0.70
N-BUTANE,%	39.57	39.27	29.84	30.21	29.42
N-BUTENE,%	0.18	0.00	0.34	0.00	0.25
TRANCE-2-BUTENE,%	0.45	0.44	0.54	0.54	0.47
CIS-2-BUTENE,%	0.52	0.44	0.34	0.46	0.19
1,3-BUTADIENE,%	0.74	0.76	0.73	0.89	0.86
METHANE,%	1.48	0.71	0.00	0.00	2.63
CARBON DIOXIDE,%	8.14	7.48	9.14	8.70	8.55
OXYGEN,%	5.48	4.66	4.92	5.84	4.92
CARBON MONOXIDE,%	2.08	4.31	7.97	7.18	5.40
NITROGEN,%	40.86	40.86	46.18	46.18	46.18
OUT FLOW,MG MOL/MIN	6.68	7.68	4.61	5.12	5.76

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	11.51	12.09	17.27	16.24	18.46
YIELD BD,%	1.66	1.71	2.01	2.47	2.39
YIELD BUTE(S)+BD,%	4.24	3.66	5.42	5.24	4.92
SELECT BD,%	14.42	14.01	11.65	15.20	12.95
SELECT BUTE(S)+BD,%	36.83	29.08	31.37	32.24	26.65

INLET CONDITIONS AND SET POINTS

RUN NO	61	62	63	64	65
TEMP,*C	400.00	400.00	400.00	400.00	400.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	32.47	27.78	27.78	27.78
OXYGEN CONC,%	25.97	25.97	27.78	27.78	27.78
NITRGN CONC,%	41.56	41.56	44.44	44.44	44.44
IN FLOW,MG MOL/MIN	7.31	8.63	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.75	1.50	2.50	2.00	1.75
OXYGEN:BUTANE	0.80	0.80	1.00	1.00	1.00
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.37	0.23	0.37	0.37	0.45
PROPELENE,%	0.00	0.33	0.00	0.43	0.00
N-BUTANE,%	29.69	29.61	23.97	23.68	23.18
N-BUTENE,%	0.00	0.21	0.00	0.00	0.22
TRANCE-2-BUTENE,%	0.73	0.42	0.33	0.37	0.17
CIS-2-BUTENE,%	0.34	0.42	0.33	0.37	0.41
1,3-BUTADIENE,%	0.70	0.98	0.77	0.78	0.86
METHANE,%	3.50	0.92	0.00	0.89	1.39
CARBON DIOXIDE,%	8.17	9.19	10.28	10.49	9.80
OXYGEN,%	4.26	5.31	3.76	3.70	2.14
CARBON MONOXIDE,%	5.06	6.22	10.79	9.62	11.99
NITROGEN,%	46.18	46.18	49.38	49.38	49.38
OUT FLOW,MG MOL/MIN	6.58	7.68	4.61	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	17.71	17.92	22.32	23.51	24.90
YIELD BD,%	1.93	2.73	2.49	2.53	2.80
YIELD BUTE(S)+BD,%	4.90	5.61	4.65	4.95	5.40
SELECT BD,%	10.91	15.23	11.15	10.71	11.24
SELECT BUTE(S)+BD,%	27.67	31.29	20.83	20.98	21.68

INLET CONDITIONS AND SET POINTS

RUN NO	66	67	68	69	70
TEMP,*C	400.00	400.00	400.00	400.00	400.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	27.78	27.78	22.83	22.83	22.83
OXYGEN CONC,%	27.78	27.78	29.68	29.68	29.68
NITRGN CONC,%	44.44	44.44	47.49	47.49	47.49
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	6.40	7.31
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.00	1.75
OXYGEN:BUTANE	1.00	1.00	1.30	1.30	1.30
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	66	67	68	69	70
ETHYLENE,%	0.55	0.67	0.00	0.34	0.38
PROPELENE,%	0.47	0.62	0.00	0.00	0.00
N-BUTANE,%	23.37	23.60	17.73	17.97	17.91
N-BUTENE,%	0.26	0.00	0.00	0.18	0.00
TRANCE-2-BUTENE,%	0.30	0.37	0.27	0.22	0.34
CIS-2-BUTENE,%	0.22	0.37	0.27	0.30	0.34
1,3-BUTADIENE,%	0.81	0.77	0.80	0.71	0.75
METHANE,%	1.42	2.10	0.00	0.00	0.86
CARBON DIOXIDE,%	10.58	10.80	11.29	11.49	10.84
OXYGEN,%	3.52	4.41	2.99	4.23	4.18
CARBON MONOXIDE,%	9.12	7.90	13.87	11.79	11.64
NITROGEN,%	49.38	49.88	52.77	52.77	52.77
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.76	6.58

CONVERSION,YIELD,SELECTIVITY

	66	67	68	69	70
CONVERSION,%	24.28	23.64	30.11	29.17	29.39
YIELD BD,%	2.63	2.48	3.15	2.79	2.94
YIELD BUTE(S)+BD,%	5.15	4.90	5.32	5.56	5.64
SELECT BD,%	10.84	10.64	10.48	9.57	10.00
SELECT BUTE(S)+BD,%	21.19	20.80	17.65	19.06	19.20

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RUN NO	71	72	73	74	75
TEMP,*C	400.00	400.00	400.00	400.00	400.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	22.83	22.63	18.72	18.72	18.72
OXYGEN CONC,%	29.68	29.68	31.26	31.26	31.26
NITRGN CONC,%	47.49	47.49	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.69	6.40
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.25	2.00
OXYGEN:BUTANE	1.30	1.30	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.50	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.47	0.00	0.00	0.00	0.27
PROPELENE,%	0.41	0.68	0.00	0.00	0.00
N-BUTANE,%	17.45	17.99	14.73	14.98	14.45
N-BUTENE,%	0.00	0.00	0.21	0.22	0.12
TRANCE-2-BUTENE,%	0.40	0.31	0.21	0.22	0.24
CIS-2-BUTENE,%	0.22	0.31	0.21	0.25	0.24
1,3-BUTADIENE,%	0.86	0.76	0.39	0.31	0.50
METHANE,%	0.37	2.20	0.00	0.00	0.80
CARBON DIOXIDE,%	11.82	11.99	13.76	13.29	13.93
OXYGEN,%	3.89	5.04	8.45	9.16	8.13
CARBON MONOXIDE,%	11.33	8.05	6.48	5.99	5.74
NITROGEN,%	52.77	52.77	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.42	5.76

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	31.20	29.09	29.16	27.98	30.54
YIELD BD,%	3.41	3.01	1.86	1.50	2.40
YIELD BUTE(S)+BD,%	5.89	5.47	4.84	4.80	5.28
SELECT BD,%	10.93	10.34	6.39	5.37	7.84
SELECT BUTE(S)+BD,%	18.86	18.81	16.59	17.17	17.28

INLET CONDITIONS AND SET POINTS

RUN NO	76	77	78	79	80
TEMP,*C	400.00	400.00	400.00	400.00	425.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	40.25
OXYGEN CONC,%	31.26	31.26	31.26	31.26	22.98
NITRGN CONC,%	50.02	50.02	50.02	50.02	36.77
IN FLOW,MG MOL/MIN	7.31	8.53	12.80	25.60	5.12
W/F,G/(MG MOL/MIN)	1.75	1.50	1.00	0.50	2.50
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	0.57
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.31	0.27	0.60	0.52	1.37
PROPELENE,%	0.42	0.61	0.15	0.00	0.00
N-BUTANE,%	14.78	14.40	14.92	14.63	38.95
N-BUTENE,%	0.22	0.26	0.23	0.21	0.32
TRANCE-2-BUTENE,%	0.22	0.18	0.36	0.21	0.47
CIS-2-BUTENE,%	0.22	0.18	0.46	0.21	0.32
1,3-BUTADIENE,%	0.46	0.39	0.39	0.46	1.52
METHANE,%	0.42	3.11	1.84	1.34	0.00
CARBON DIOXIDE,%	12.29	14.84	13.60	14.26	7.66
OXYGEN,%	10.07	8.93	11.20	8.87	6.36
CARBON MONOXIDE,%	5.01	1.26	0.78	3.72	2.19
NITROGEN,%	55.58	55.58	55.58	55.58	40.86
OUT FLOW,MG MOL/MIN	6.68	7.68	11.62	23.04	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	28.96	30.79	28.27	29.64	12.91
YIELD BD,%	2.23	1.86	1.87	2.20	3.40
YIELD BUTE(S)+BD,%	5.39	4.85	6.93	5.17	5.87
SELECT BD,%	7.69	6.06	6.61	7.41	26.33
SELECT BUTE(S)+BD,%	18.62	15.76	24.51	17.43	45.51

INLET CONDITIONS AND SET POINTS

RUN NO	81	82	83	84	85
TEMP,*C	425.00	425.00	425.00	425.00	425.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	40.25	40.25	40.25	40.25	40.25
OXYGEN CONC,%	22.98	22.98	22.98	22.98	22.98
NITRGN CONC,%	36.77	36.77	36.77	36.77	36.77
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	8.53	12.80
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	1.00
OXYGEN:BUTANE	0.57	0.57	0.57	0.57	0.57
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	1.29	0.86	0.27	1.06	2.32
PROPELENE,%	0.00	0.56	0.90	0.84	0.66
N-BUTANE,%	38.89	38.84	38.69	38.98	38.80
N-BUTENE,%	0.32	0.38	0.49	0.00	0.38
TRANCE-2-BUTENE,%	0.45	0.38	0.28	0.53	0.41
CIS-2-BUTENE,%	0.45	0.38	0.48	0.53	0.41
1,3-BUTADIENE,%	1.56	1.50	1.34	1.32	1.30
METHANE,%	0.00	0.00	0.75	1.50	3.41
CARBON DIOXIDE,%	8.43	9.47	8.57	9.25	10.53
OXYGEN,%	6.55	6.70	6.17	5.61	0.92
CARBON MONOXIDE,%	1.20	0.86	1.19	0.00	0.00
NITROGEN,%	40.86	40.86	40.86	40.86	40.86
OUT FLOW,MG MOL/MIN	5.42	5.76	6.68	7.68	11.52

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	13.03	13.45	13.48	12.83	13.24
YIELD BD,%	3.48	3.35	3.00	2.96	2.90
YIELD BUTE(S)+BD,%	6.20	5.82	5.78	5.35	5.60
SELECT BD,%	26.72	25.46	22.22	23.06	21.92
SELECT BUTE(S)+BD,%	47.57	45.02	42.87	41.68	42.26

INLET CONDITIONS AND SET POINTS

RUN NO	86	87	88	89	90
TEMP,*C	425.00	425.00	425.00	425.00	425.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	32.47	32.47	32.47	32.47
OXYGEN CONC,%	25.97	25.97	25.97	25.97	25.97
NITRGN CONC,%	41.56	41.56	41.56	41.56	41.56
IN FLOW,MG MOL/MIN	5.12	5.69	6.40	7.31	8.53
W/F,G/(MG MOL/MIN)	2.50	2.25	2.00	1.75	1.50
OXYGEN:BUTANE	0.80	0.80	0.80	0.80	0.80
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	86	87	88	89	90
ETHYLENE,%	0.00	1.04	0.75	0.93	1.36
PROPELENE,%	0.00	0.00	0.27	0.49	1.23
N-BUTANE,%	29.26	29.45	29.03	28.99	29.09
N-BUTENE,%	0.00	0.36	0.00	0.31	0.55
TRANCE-2-BUTENE,%	0.68	0.47	0.60	0.31	0.55
CIS-2-BUTENE,%	0.68	0.36	0.60	0.31	0.55
1,3-BUTADIENE,%	1.46	1.64	1.84	1.69	1.60
METHANE,%	0.00	0.00	0.00	2.67	3.70
CARBON DIOXIDE,%	8.85	8.96	8.67	8.17	10.87
OXYGEN,%	5.75	7.44	6.99	5.32	4.33
CARBON MONOXIDE,%	7.15	4.09	5.08	3.61	0.00
NITROGEN,%	46.18	46.18	46.18	46.18	46.18
OUT FLOW,MG MOL/MIN	4.61	5.12	5.76	6.68	7.68

CONVERSION,YIELD,SELECTIVITY

	86	87	88	89	90
CONVERSION,%	18.89	18.86	19.52	19.63	19.35
YIELD BD,%	4.04	4.65	5.10	4.70	4.45
YIELD BUTE(S)+BD,%	7.80	7.87	8.40	7.31	8.99
SELECT BD,%	21.37	24.78	26.13	23.94	22.99
SELECT BUTE(S)+BD,%	41.30	42.88	43.04	37.26	46.44

RUN NO	91	92	93	94	95
TEMP,*C	425.00	425.00	425.00	425.00	425.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	18.72	18.72	18.72	18.72
OXYGEN CONC,%	25.97	31.26	31.26	31.26	31.26
NITRGN CONC,%	41.56	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	12.80	5.12	5.69	5.40	7.31
W/F,G/(MG MOL/MIN)	1.00	2.50	2.25	2.00	1.75
OXYGEN:BUTANE	0.80	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	91	92	93	94	95
ETHYLENE,%	1.07	0.00	0.00	1.56	0.00
PROPELENE,%	1.35	0.00	0.00	0.00	0.00
N-BUTANE,%	29.46	14.42	14.39	14.11	14.79
1-BUTENE,%	0.28	0.23	0.16	0.12	0.26
TRANCE-2-BUTENE,%	0.28	0.40	0.48	0.50	0.51
CIS-2-BUTENE,%	0.51	0.61	0.16	0.50	0.26
1,3-BUTADIENE,%	1.60	0.74	0.94	0.97	0.98
METHANE,%	1.83	0.00	0.00	0.63	1.80
CARBON DIOXIDE,%	7.97	14.28	15.09	13.78	14.32
OXYGEN,%	9.46	10.09	9.63	11.89	11.51
CARBON MONOXIDE,%	0.00	3.77	3.57	0.86	0.00
NITROGEN,%	46.18	55.58	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	11.52	4.61	5.12	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

	91	92	93	94	95
CONVERSION,%	18.33	30.69	30.84	32.17	28.88
YIELD BD,%	4.43	3.64	4.53	4.66	4.72
YIELD BUTE(S)+BD,%	7.41	8.99	8.41	10.06	9.63
SELECT BD,%	24.17	11.64	14.59	14.48	16.36
SELECT BUTE(S)+BD,%	40.43	29.31	27.28	31.28	33.36

INLET CONDITIONS AND SET POINTS

RUN NO	96	97	98	99	100
TEMP,*C	425.00	425.00	440.00	440.00	440.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITROGEN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	8.53	12.80	5.12	5.69	6.40
W/F,G/(MG MOL/MIN)	1.50	1.00	2.50	2.25	2.00
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.90	1.16	0.00	0.00	0.62
PROPELENE,%	0.16	0.25	0.00	0.00	0.00
N-BUTANE,%	14.32	14.47	14.30	14.23	14.12
N-BUTENE,%	0.29	0.00	0.00	0.35	0.34
TRANCE-2-BUTENE,%	0.29	0.35	0.32	0.35	0.33
CIS-2-BUTENE,%	0.29	0.70	0.32	0.00	0.33
1,3-BUTADIENE,%	1.01	1.03	1.33	1.41	1.36
METHANE,%	0.42	0.99	0.00	0.00	0.00
CARBON DIOXIDE,%	14.79	14.23	14.76	14.30*	13.93
OXYGEN,%	11.09	11.24	10.06	10.25	11.32
CARBON MONOXIDE,%	0.85	0.00	3.33	3.52	2.06
NITROGEN,%	55.58	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	7.68	11.52	4.61	5.42	5.76

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	31.13	30.44	31.24	31.60	32.10
YIELD BD,%	4.83	4.97	6.40	6.79	6.54
YIELD BUTE(S)+BD,%	9.08	10.02	9.50	10.18	11.39
SELECT BD,%	15.53	16.32	20.49	21.49	20.37
SELECT BUTE(S)+BD,%	29.17	32.91	30.40	32.20	35.48

INLET CONDITIONS AND SET POINTS

RUN NO	101	102	103	104	105
TEMP,*C	440.00	440.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	40.25	40.25	40.25
OXYGEN CONC,%	31.26	31.26	22.98	22.98	22.98
NITRGN CONC,%	50.02	50.02	36.77	36.77	36.77
IN FLOW,MG MOL/MIN	7.31	8.53	5.12	5.40	7.31
W/F,G/(MG MOL/MIN)	1.75	1.50	2.50	2.00	1.75
OXYGEN:BUTANE	1.67	1.67	0.57	0.57	0.57
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	101	102	103	104	105
ETHYLENE,%	1.10	0.59	0.15	0.00	0.00
PROPELENE,%	0.42	0.00	0.00	0.00	0.00
N-BUTANE,%	14.49	14.32	38.22	38.60	38.73
N-BUTENE,%	0.42	0.44	0.49	0.33	0.32
TRANCE-2-BUTENE,%	0.42	0.25	0.64	0.42	0.40
CIS-2-BUTENE,%	0.42	0.25	0.49	0.39	0.26
1,3-BUTADIENE,%	1.30	1.35	2.02	2.24	2.21
METHANE,%	1.57	2.63	0.00	0.00	0.00
CARBON DIOXIDE,%	14.81	13.79	8.93	8.53	10.06
OXYGEN,%	9.48	10.80	5.00	5.20	6.03
CARBON MONOXIDE,%	0.00	0.00	2.19	2.43	1.13
NITROGEN,%	55.58	55.68	40.86	40.86	40.86
OUT FLOW,MG MOL/MIN	6.68	7.58	4.61	5.75	6.58

CONVERSION,YIELD,SELECTIVITY

	101	102	103	104	105
CONVERSION,%	30.35	31.43	14.52	13.70	13.40
YIELD BD,%	6.25	6.47	4.53	5.00	4.95
YIELD BUTE(S)+BD,%	12.29	11.00	8.13	7.57	7.14
SELECT BD,%	20.58	20.79	31.17	35.51	36.92
SELECT BUTE(S)+BD,%	40.49	35.83	56.00	55.26	53.31

INLET CONDITIONS AND SET POINTS

RUN NO	105	107	108	109	110
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	40.25	40.25	40.25	32.47	32.47
OXYGEN CONC,%	22.98	22.98	22.98	25.97	25.97
NITRGN CONC,%	36.77	36.77	36.77	41.55	41.55
IN FLOW,MG MOL/MIN	8.53	12.80	25.60	5.12	6.40
W/F,G/(MG MOL/MIN)	1.50	1.00	0.50	2.50	2.00
OXYGEN:BUTANE	0.57	0.57	0.57	0.80	0.80
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.00	0.66	0.66	0.15	0.00
PROPELENE,%	0.00	0.46	0.59	0.00	0.00
N-BUTANE,%	38.45	38.95	38.41	28.87	28.83
1-BUTENE,%	0.31	0.29	0.32	0.85	0.24
TRANCE-2-BUTENE,%	0.39	0.40	0.00	0.52	0.31
CIS-2-BUTENE,%	0.35	0.32	0.65	0.48	0.31
1,3-BUTADIENE,%	2.34	1.91	2.01	1.31	2.22
METHANE,%	0.00	0.65	0.66	0.00	0.00
CARBON DIOXIDE,%	8.60	9.87	9.51	10.85	10.74
OXYGEN,%	5.81	5.73	6.30	5.72	5.23
CARBON MONOXIDE,%	2.89	0.00	0.02	5.59	5.96
NITROGEN,%	40.86	40.86	40.86	45.18	46.18
OUT FLOW,MG MOL/MIN	7.68	11.52	23.04	4.61	5.76

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	14.01	12.01	14.11	19.98	20.07
YIELD BD,%	5.24	4.27	4.50	3.62	6.15
YIELD BUTE(S)+BD,%	7.60	6.62	6.68	8.73	8.50
SELECT BD,%	37.39	33.11	31.90	18.13	30.66
SELECT BUTE(S)+BD,%	54.20	50.63	47.35	43.68	42.36

INLET CONDITIONS AND SET POINTS

RUN NO	111	112	113	114	115
TEMP, *C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	32.47	32.47	32.47	27.78
OXYGEN CONC,%	25.97	25.97	25.97	25.97	27.78
NITRGN CONC,%	41.56	41.56	41.56	41.56	44.44
IN FLOW,MG MOL/MIN	7.31	8.63	12.80	25.60	5.12
W/F,G/(MG MOL/MIN)	1.75	1.60	1.00	0.50	2.50
OXYGEN:BUTANE	0.80	0.80	0.80	0.80	1.00
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.00	0.00	0.29	0.91	0.00
PROPELENE,%	0.00	0.00	0.51	0.32	0.00
N-BUTANE,%	29.25	28.66	29.00	23.13	22.25
N-BUTENE,%	0.28	0.23	0.34	0.42	0.28
TRANCE-2-BUTENE,%	0.39	0.31	0.35	0.42	0.56
CIS-2-BUTENE,%	0.31	0.27	0.42	0.38	0.56
1,3-BUTADIENE,%	1.97	1.94	1.95	1.72	1.92
METHANE,%	0.00	0.00	1.53	2.33	0.00
CARBON DIOXIDE,%	10.33	11.80	11.84	11.99	13.16
OXYGEN,%	6.12	3.77	7.01	4.30	3.81
CARBON MONOXIDE,%	5.18	6.83	0.58	2.89	8.10
NITROGEN,%	45.18	46.18	46.18	45.18	49.38
OUT FLOW,MG MOL/MIN	6.58	7.68	11.52	23.04	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	18.93	20.66	19.62	22.03	27.92
YIELD BD,%	5.45	5.39	5.39	4.76	6.21
YIELD BUTE(S)+BD,%	8.18	7.65	8.49	8.17	10.71
SELECT BD,%	28.82	26.20	27.49	21.63	22.23
SELECT BUTE(S)+BD,%	43.22	37.20	43.28	37.11	38.35

INLET CONDITIONS AND SET POINTS

RUN NO	115	117	118	119	120
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	27.78	27.78	27.78	27.78	27.78
OXYGEN CONC,%	27.78	27.78	27.78	27.78	27.78
NITRGN CONC,%	44.44	44.44	44.44	44.44	44.44
IN FLOW,MG MOL/MIN	6.40	7.31	8.53	12.80	25.60
W/F,G/(MG MOL/MIN)	2.00	1.75	1.50	1.00	0.50
OXYGEN:BUTANE	1.00	1.00	1.00	1.00	1.00
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	115	117	118	119	120
ETHYLENE,%	0.15	0.00	0.00	0.38	0.85
PROPELENE,%	0.00	0.00	0.00	0.34	1.07
N-BUTANE,%	22.91	23.45	23.02	22.14	21.41
N-BUTENE,%	0.31	0.46	0.29	0.44	0.25
TRANCE-2-BUTENE,%	0.31	0.69	0.00	0.24	0.60
CIS-2-BUTENE,%	0.31	0.78	1.11	0.56	0.61
1,3-BUTADIENE,%	2.00	1.98	1.93	2.05	1.28
METHANE,%	0.00	0.00	0.00	1.39	1.67
CARBON DIOXIDE,%	11.80	14.27	11.57	11.57	12.02
OXYGEN,%	4.83	8.01	6.22	4.51	2.59
CARBON MONOXIDE,%	8.00	1.89	6.47	5.99	8.27
NITROGEN,%	49.38	49.38	49.38	49.38	49.38
OUT FLOW,MG MOL/MIN	6.76	6.58	7.68	11.62	23.04

CONVERSION,YIELD,SELECTIVITY

	115	117	118	119	120
CONVERSION,%	25.76	25.01	25.41	28.26	30.64
YIELD BD,%	6.48	6.40	6.24	6.54	4.14
YIELD BUTE(S)+BD,%	9.48	12.82	10.79	10.66	8.87
SELECT BD,%	25.16	25.60	24.55	23.49	13.50
SELECT BUTE(S)+BD,%	36.81	49.28	42.48	37.72	28.94

INLET CONDITIONS AND SET POINTS

RUN NO	121	122	123	124	125
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	22.83	22.83	22.83	22.83	22.83
OXYGEN CONC,%	29.68	29.68	29.58	29.68	29.68
NITRGN CONC,%	47.49	47.49	47.49	47.49	47.49
IN FLOW,MG MOL/MIN	5.12	6.40	7.31	8.53	12.80
W/F,G/(MG MOL/MIN)	2.50	2.00	1.75	1.50	1.00
OXYGEN:BUTANE	1.30	1.30	1.30	1.30	1.30
NITROGEN:OXYGEN	1.60	1.60	1.50	1.50	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.00	0.00	0.15	0.31	0.00
PROPELENE,%	0.00	0.00	0.00	0.00	0.28
N-BUTANE,%	17.79	17.69	17.90	17.61	17.56
N-BUTENE,%	0.39	0.26	0.44	0.29	0.26
TRANCE-2-BUTENE,%	0.27	0.26	0.27	0.29	0.45
CIS-2-BUTENE,%	0.26	0.46	0.54	0.29	0.45
1,3-BUTADIENE,%	1.78	1.78	1.84	1.78	1.86
METHANE,%	0.00	0.00	0.00	0.50	1.15
CARBON DIOXIDE,%	13.78	13.47	12.34	14.35	12.97
OXYGEN,%	7.26	7.41	8.86	5.92	8.09
CARBON MONOXIDE,%	5.70	6.21	4.90	4.87	4.15
NITROGEN,%	52.77	52.77	52.77	52.77	52.77
OUT FLOW,MG MOL/MIN	4.61	5.76	6.58	7.68	11.52

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	29.85	30.29	29.44	30.57	30.79
YIELD BD,%	7.01	7.02	7.25	7.04	7.35
YIELD BUTE(S)+BD,%	10.65	10.89	12.16	10.51	11.94
SELECT BD,%	23.49	23.19	24.61	23.01	23.86
SELECT BUTE(S)+BD,%	35.69	35.97	41.28	34.39	38.77

RUN NO	126	127	128	129	130
TEMP,*C	450.00	450.00	450.00	450.00	450.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	22.83	18.72	18.72	18.72	18.72
OXYGEN CONC,%	29.68	31.26	31.26	31.26	31.26
NITRGN CONC,%	47.49	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	25.60	5.12	6.40	7.31	8.53
W/F,G/(MG MOL/MIN)	0.50	2.50	2.00	1.75	1.50
OXYGEN:BUTANE	1.30	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	1.69	0.00	0.00	0.40	0.30
PROPELENE,%	0.36	0.00	0.00	0.00	0.00
N-BUTANE,%	15.13	14.04	14.11	14.54	14.09
N-BUTENE,%	0.28	0.24	0.28	0.25	0.31
TRANCE-2-BUTENE,%	0.39	0.32	0.40	0.32	0.31
CIS-2-BUTENE,%	0.14	0.32	0.32	0.32	0.31
1,3-BUTADIENE,%	1.13	1.86	1.50	1.48	1.56
METHANE,%	2.44	0.00	0.00	0.50	0.59
CARBON DIOXIDE,%	13.30	15.06	14.93	14.50	12.84
OXYGEN,%	2.36	10.03	11.08	12.42	11.28
CARBON MONOXIDE,%	9.02	3.07	1.79	0.00	2.82
NITROGEN,%	52.77	55.68	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	23.04	4.61	5.76	6.58	7.68

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	36.43	32.61	32.45	30.09	32.25
YIELD BD,%	4.47	6.62	7.23	7.11	7.48
YIELD BUTE(S)+BD,%	7.62	10.73	12.05	11.36	12.00
SELECT BD,%	12.26	20.04	22.48	23.64	23.19
SELECT BUTE(S)+BD,%	20.92	32.89	37.47	37.76	37.20

INLET CONDITIONS AND SET POINTS

RUN NO	131	132	133	134	135
TEMP,*C	450.00	450.00	460.00	460.00	460.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	12.80	25.60	5.12	5.69	6.40
W/F,G/(MG MOL/MIN)	1.00	0.50	2.50	2.25	2.00
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.22	1.69	0.45	0.00	0.00
PROPELENE,%	0.36	0.00	0.25	0.00	0.00
N-BUTANE,%	14.73	13.91	13.48	14.38	13.91
N-BUTENE,%	0.29	0.32	0.42	0.43	0.37
TRANCE-2-BUTENE,%	0.29	0.40	0.63	0.43	0.48
CIS-2-BUTENE,%	0.29	0.24	0.47	0.43	0.17
1,3-BUTADIENE,%	1.46	1.51	1.28	1.19	1.39
METHANE,%	3.53	3.26	1.32	0.00	0.00
CARBON DIOXIDE,%	12.04	13.76	15.24	15.06	14.09
OXYGEN,%	11.21	9.83	10.89	11.81	10.20
CARBON MONOXIDE,%	0.00	0.00	0.00	0.69	3.81
NITRGEN,%	55.58	55.58	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	11.52	23.04	4.61	5.42	5.76

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	29.20	33.11	35.21	30.86	33.10
YIELD BD,%	7.02	7.28	6.16	5.70	6.67
YIELD BUTE(S)+BD,%	11.23	11.89	13.44	11.93	11.58
SELECT BD,%	24.05	21.98	17.51	18.47	20.14
SELECT BUTE(S)+BD,%	38.47	35.90	38.18	38.65	35.00

INLET CONDITIONS AND SET POINTS

RUN NO	136	137	138	139	140
TEMP,*C	460.00	460.00	460.00	460.00	475.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	40.25
OXYGEN CONC,%	31.26	31.26	31.26	31.26	22.98
NITRGN CONC,%	50.02	50.02	50.02	50.02	36.77
IN FLOW,MG MOL/MIN	7.31	8.53	12.80	25.60	5.12
W/F,G/(MG MOL/MIN)	1.75	1.50	1.00	0.50	2.50
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	0.57
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.00	0.00	1.32	1.80	0.00
PROPELENE,%	0.00	0.00	0.00	0.99	0.00
N-BUTANE,%	14.22	13.69	14.33	13.08	37.31
N-BUTENE,%	0.00	0.14	0.41	0.25	0.00
TRANCE-2-BUTENE,%	0.38	0.50	0.29	0.42	0.60
CIS-2-BUTENE,%	0.38	0.50	0.29	0.25	0.60
1,3-BUTADIENE,%	1.42	1.43	1.36	1.12	1.95
METHANE,%	0.60	0.00	2.47	1.39	0.00
CARBON DIOXIDE,%	14.82	16.79	15.60	14.31	13.05
OXYGEN,%	10.42	9.99	8.47	10.37	1.67
CARBON MONOXIDE,%	2.19	1.89	0.00	0.44	3.96
NITROGEN,%	55.58	55.58	55.58	55.58	40.86
OUT FLOW,MG MOL/MIN	6.68	7.68	11.52	23.04	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	31.65	34.18	31.13	37.09	16.56
YIELD BD,%	6.81	6.87	6.53	5.37	4.35
YIELD BUTE(S)+BD,%	10.49	12.33	11.28	9.79	7.05
SELECT BD,%	21.52	20.08	20.99	14.48	26.27
SELECT BUTE(S)+BD,%	33.14	36.09	36.25	25.38	42.58

RUN NO	141	142	143	144	145
TEMP,*C	475.00	475.00	475.00	475.00	475.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	40.25	40.25	40.25	40.25	32.47
OXYGEN CONC,%	22.98	22.98	22.98	22.98	25.97
NITRGN CONC,%	36.77	36.77	36.77	36.77	41.56
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	8.53	5.12
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	2.50
OXYGEN:BUTANE	0.57	0.57	0.57	0.57	0.80
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.38	3.12	1.73	2.02	0.00
PROPELENE,%	0.00	1.33	0.74	0.70	0.00
N-BUTANE,%	38.28	37.78	38.71	37.84	27.65
N-BUTENE,%	0.00	0.28	0.50	0.25	0.34
TRANCE-2-BUTENE,%	0.53	0.23	0.50	0.77	0.34
CIS-2-BUTENE,%	0.53	0.63	0.50	0.38	0.34
1,3-BUTADIENE,%	2.22	2.05	1.77	2.02	2.06
METHANE,%	0.00	0.00	1.74	0.69	0.00
CARBON DIOXIDE,%	11.78	11.70	12.80	11.93	13.29
OXYGEN,%	5.31	2.02	0.16	2.63	1.75
CARBON MONOXIDE,%	0.11	0.00	0.00	0.00	8.04
NITROGEN,%	40.86	40.86	40.86	40.86	46.18
OUT FLOW,MG MOL/MIN	5.42	5.76	6.58	7.68	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	14.39	15.63	13.44	15.88	23.34
YIELD BD,%	4.97	4.69	3.96	4.53	5.70
YIELD BUTE(S)+BD,%	7.32	7.44	7.29	7.65	8.56
SELECT BD,%	34.50	29.65	29.44	29.43	24.42
SELECT BUTE(S)+BD,%	50.86	46.01	54.25	49.75	36.68

INLET CONDITIONS AND SET POINTS

RUN NO	146	147	148	149	150
TEMP,*C	475.00	475.00	475.00	475.00	475.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	32.47	32.47	32.47	18.72
OXYGEN CONC,%	25.97	25.97	25.97	25.97	31.26
NITRGN CONC,%	41.56	41.56	41.56	41.56	50.02
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	8.53	5.12
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	2.50
OXYGEN:BUTANE	0.80	0.80	0.80	0.80	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

	146	147	148	149	150
ETHYLENE,%	1.28	1.87	1.95	0.00	0.00
PROPELENE,%	0.00	0.19	1.28	1.09	0.00
N-BUTANE,%	27.43	28.28	27.63	28.27	13.27
N-BUTENE,%	0.55	0.61	0.42	0.31	0.35
TRANCE-2-BUTENE,%	0.63	0.58	0.83	0.31	0.31
CIS-2-BUTENE,%	0.67	0.58	0.42	0.60	0.31
1,3-BUTADIENE,%	1.86	1.59	1.79	1.73	1.28
METHANE,%	0.00	0.00	1.28	0.64	0.00
CARBON DIOXIDE,%	12.53	13.38	13.74	14.43	16.31
OXYGEN,%	4.25	6.42	4.49	5.83	7.77
CARBON MONOXIDE,%	4.62	0.41	0.00	1.12	4.82
NITROGEN,%	46.18	46.18	46.18	46.18	55.58
OUT FLOW,MG MOL/MIN	5.12	5.76	6.63	7.68	4.61

CONVERSION,YIELD,SELECTIVITY

	146	147	148	149	150
CONVERSION,%	23.95	21.62	23.41	21.64	36.20
YIELD BD,%	5.16	4.41	4.97	4.80	6.17
YIELD BUTE(S)+BD,%	10.29	9.07	9.57	8.16	10.80
SELECT BD,%	21.56	20.39	21.24	22.20	17.05
SELECT BUTE(S)+BD,%	42.96	41.94	40.89	37.71	29.83

INLET CONDITIONS AND SET POINTS

RUN NO	151	152	153	154	155
TEMP,*C	475.00	475.00	475.00	475.00	500.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	40.25
OXYGEN CONC,%	31.26	31.26	31.26	31.26	22.98
NITRGN CONC,%	50.02	50.02	50.02	50.02	36.77
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	9.53	5.12
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	2.50
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	0.57
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	0.17	0.41	0.00	1.61	3.01
PROPELENE,%	0.00	0.00	0.29	0.95	0.64
N-BUTANE,%	13.49	13.60	13.83	13.16	35.30
N-BUTENE,%	0.00	0.34	0.44	0.33	0.00
TRANCE-2-BUTENE,%	0.55	0.34	0.39	0.33	0.54
CIS-2-BUTENE,%	0.44	0.34	0.33	0.33	0.54
1,3-BUTADIENE,%	1.36	1.32	1.29	1.36	2.02
METHANE,%	0.00	0.59	1.27	0.98	0.00
CARBON DIOXIDE,%	17.28	16.66	17.39	15.47	15.15
OXYGEN,%	8.92	9.46	9.20	9.91	0.00
CARBON MONOXIDE,%	2.22	1.36	0.00	0.00	2.17
NITROGEN,%	55.58	55.68	55.58	55.58	40.86
OUT FLOW,MG MOL/MIN	5.42	5.76	6.58	7.68	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	35.14	34.60	33.52	35.74	21.06
YIELD BD,%	6.52	6.35	6.21	6.53	4.52
YIELD BUTE(S)+BD,%	11.29	11.24	11.79	11.26	6.94
SELECT BD,%	18.55	18.36	18.53	17.78	21.46
SELECT BUTE(S)+BD,%	32.14	32.49	35.19	30.65	32.95

INLET CONDITIONS AND SET POINTS

RUN NO	156	157	158	159	160
TEMP,*C	500.00	500.00	500.00	500.00	500.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	40.25	40.25	40.25	40.25	32.47
OXYGEN CONC,%	22.98	22.98	22.98	22.98	25.97
NITRGN CONC,%	36.77	36.77	36.77	36.77	41.56
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	8.53	5.12
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	2.50
OXYGEN:BUTANE	0.57	0.67	0.57	0.57	0.80
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	2.44	1.96	3.37	3.15	1.81
PROPELENE,%	0.57	1.48	1.20	1.68	0.00
N-BUTANE,%	35.44	36.25	34.74	35.31	27.30
N-BUTENE,%	0.00	0.28	0.68	0.29	0.29
TRANCE-2-BUTENE,%	0.87	0.83	0.85	0.67	0.49
CIS-2-BUTENE,%	0.87	0.28	0.68	0.41	0.29
1,3-BUTADIENE,%	1.88	1.63	1.93	1.92	1.70
METHANE,%	0.00	0.00	2.11	1.99	0.00
CARBON DIOXIDE,%	14.23	10.82	12.44	13.59	13.81
OXYGEN,%	1.06	2.69	1.15	0.22	1.54
CARBON MONOXIDE,%	1.77	3.03	0.00	0.00	6.60
NITROGEN,%	40.86	40.86	40.86	40.86	46.18
OUT FLOW,MG MOL/MIN	5.42	5.76	6.58	7.68	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	20.74	18.04	22.32	21.03	24.33
YIELD BD,%	4.21	3.42	4.31	4.29	4.71
YIELD BUTE(S)+BD,%	8.12	6.53	9.27	7.37	7.68
SELECT BD,%	20.28	18.09	19.30	20.40	19.37
SELECT BUTE(S)+BD,%	39.13	34.48	41.52	35.02	31.58

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INLET CONDITIONS AND SET POINTS

RUN NO	161	162	163	164	165
TEMP,*C	500.00	500.00	500.00	500.00	500.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	32.47	32.47	32.47	32.47	27.78
OXYGEN CONC,%	25.97	25.97	25.97	25.97	27.78
NITROGEN CONC,%	41.56	41.56	41.56	41.56	44.44
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	8.53	5.12
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	2.50
OXYGEN:BUTANE	0.80	0.80	0.80	0.80	1.00
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	1.67	2.01	1.15	2.00	0.84
PROPYLENE,%	0.58	0.00	1.18	0.65	0.00
N-BUTANE,%	25.67	27.01	26.84	26.27	20.32
N-BUTENE,%	0.40	0.29	0.27	0.45	0.24
TRANCE-2-BUTENE,%	0.32	0.67	0.44	0.29	0.44
CIS-2-BUTENE,%	0.32	0.35	0.32	0.29	0.44
1,3-BUTADIENE,%	1.73	1.46	1.56	1.63	1.54
METHANE,%	0.00	0.00	0.38	0.69	0.00
CARBON DIOXIDE,%	14.22	11.03	13.74	15.15	15.30
OXYGEN,%	0.66	0.86	1.31	0.00	0.00
CARBON MONOXIDE,%	7.25	9.24	5.64	5.76	14.57
NITROGEN,%	46.18	46.18	45.18	45.18	49.38
OUT FLOW,MG MOL/MIN	5.12	5.76	6.58	7.68	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	25.08	25.14	25.50	27.17	34.17
YIELD BD,%	4.78	4.06	4.33	4.52	4.98
YIELD BUTE(S)+BD,%	7.68	7.68	7.17	7.40	8.62
SELECT BD,%	18.34	16.15	16.90	16.64	14.59
SELECT BUTE(S)+BD,%	29.46	30.65	28.00	27.22	25.22

INLET CONDITIONS AND SET POINTS

RUN NO	166	167	168	169	170
TEMP,*C	500.00	500.00	500.00	500.00	500.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	27.78	27.78	27.78	27.78	22.83
OXYGEN CONC,%	27.78	27.78	27.78	27.78	29.68
NITRGN CONC,%	44.44	44.44	44.44	44.44	47.49
IN FLOW,MG MOL/MIN	6.40	7.31	8.53	12.80	5.12
W/F,G/(MG MOL/MIN)	2.00	1.75	1.50	1.00	2.50
OXYGEN:BUTANE	1.00	1.00	1.00	1.00	1.30
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	1.13	2.77	2.77	1.41	0.88
PROPELENE,%	0.67	0.82	1.51	1.57	0.40
N-BUTANE,%	20.54	21.34	20.13	20.61	15.44
N-BUTENE,%	0.35	0.00	0.42	0.34	0.00
TRANCE-2-BUTENE,%	0.39	0.61	0.47	0.60	0.49
CIS-2-BUTENE,%	0.38	0.60	0.47	0.56	0.49
1,3-BUTADIENE,%	1.47	1.36	1.58	1.59	1.33
METHANE,%	1.45	0.96	1.39	1.60	0.00
CARBON DIOXIDE,%	15.62	15.18	15.28	15.56	16.61
OXYGEN,%	0.00	2.99	2.49	2.79	0.67
CARBON MONOXIDE,%	9.61	4.08	4.39	3.99	10.92
NITROGEN,%	49.38	49.38	49.38	49.38	52.77
OUT FLOW,MG MOL/MIN	5.76	6.58	7.68	11.62	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	33.44	30.87	34.77	33.21	39.15
YIELD BD,%	4.75	4.42	5.12	5.14	5.25
YIELD BUTE(S)+BD,%	8.38	8.00	9.56	9.97	9.09
SELECT BD,%	14.20	14.30	14.71	15.47	13.41
SELECT BUTE(S)+BD,%	25.05	25.91	27.49	30.01	23.21

INLET CONDITIONS AND SET POINTS

RUN NO	171	172	173	174	175
TEMP,*C	500.00	500.00	500.00	500.00	500.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	22.83	22.83	22.83	22.83	18.72
OXYGEN CONC,%	29.68	29.68	29.68	29.68	31.26
NITRGN CONC,%	47.49	47.49	47.49	47.49	50.02
IN FLOW,MG MOL/MIN	5.40	7.31	8.53	12.80	5.12
W/F,G/(MG MOL/MIN)	2.00	1.75	1.50	1.00	2.50
OXYGEN:BUTANE	1.30	1.30	1.30	1.30	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	1.05	1.45	1.02	1.32	0.58
PROPELENE,%	0.49	0.00	0.58	0.72	0.00
N-BUTANE,%	15.08	15.18	14.73	15.04	12.25
N-BUTENE,%	0.36	0.33	0.33	0.33	0.23
TRANCE-2-BUTENE,%	0.36	0.42	0.35	0.42	0.53
CIS-2-BUTENE,%	0.36	0.34	0.35	0.36	0.23
1,3-BUTADIENE,%	1.41	1.39	1.50	1.41	1.02
METHANE,%	0.00	0.72	1.12	1.45	0.00
CARBON DIOXIDE,%	15.02	17.14	16.16	16.55	16.27
OXYGEN,%	0.55	0.17	0.00	1.24	4.57
CARBON MONOXIDE,%	11.54	10.11	11.36	3.39	8.76
NITROGEN,%	52.77	52.77	52.77	52.77	55.58
OUT FLOW,MG MOL/MIN	5.76	6.58	7.63	11.62	4.61

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	40.55	40.17	41.95	40.71	41.12
YIELD BD,%	5.56	5.48	5.91	5.57	4.91
YIELD BUTE(S)+BD,%	9.88	9.75	9.99	9.97	9.55
SELECT BD,%	13.71	13.63	14.09	13.69	11.93
SELECT BUTE(S)+BD,%	24.35	24.27	23.82	24.48	23.47

RUN NO	176	177	178	179	180
TEMP,*C	500.00	500.00	500.00	500.00	500.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	5.00	5.00	5.00	5.00
CAT WT,G	12.80	12.80	12.80	12.80	12.80
BUTANE CONC,%	18.72	18.72	18.72	18.72	18.72
OXYGEN CONC,%	31.26	31.26	31.26	31.26	31.26
NITRGN CONC,%	50.02	50.02	50.02	50.02	50.02
IN FLOW,MG MOL/MIN	5.69	6.40	7.31	8.53	12.80
W/F,G/(MG MOL/MIN)	2.25	2.00	1.75	1.50	1.00
OXYGEN:BUTANE	1.67	1.67	1.67	1.67	1.67
NITROGEN:OXYGEN	1.60	1.60	1.60	1.60	1.60

OUTLET CONCENTRATIONS

ETHYLENE,%	1.61	1.83	1.84	3.01	2.27
PROPELENE,%	0.55	0.00	0.53	1.25	0.80
N-BUTANE,%	12.14	12.40	11.91	12.14	12.06
N-BUTENE,%	0.34	0.35	0.37	0.34	0.00
TRANCE-2-BUTENE,%	0.34	0.35	0.00	0.34	0.69
CIS-2-BUTENE,%	0.34	0.35	0.74	0.34	0.36
1,3-BUTADIENE,%	1.07	1.09	1.05	1.08	1.11
METHANE,%	0.00	0.43	1.63	0.97	0.77
CARBON DIOXIDE,%	17.10	18.34	17.04	17.31	16.76
OXYGEN,%	6.66	6.46	6.33	7.65	7.75
CARBON MONOXIDE,%	4.27	3.63	2.97	0.00	1.85
NITROGEN,%	55.58	55.58	55.58	55.58	55.58
OUT FLOW,MG MOL/MIN	5.42	5.76	6.58	7.68	11.52

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	41.62	40.40	42.74	41.63	42.02
YIELD BD,%	5.15	5.26	5.05	5.17	5.35
YIELD BUTE(S)+BD,%	10.09	10.28	10.39	10.06	10.37
SELECT BD,%	12.38	13.02	11.82	12.42	12.73
SELECT BUTE(S)+BD,%	24.24	25.46	24.30	24.16	24.68

RUN NO	181	182	183	184	185
TEMP,*C	500.00	0.00	0.00	0.00	0.00
ACTIVE COMPONENT	BETA	BETA	BETA	BETA	BETA
CAT CONC,MOL/100 MOL	5.00	0.00	0.00	0.00	0.00
CAT WT,G	12.80	0.00	0.00	0.00	0.00
BUTANE CONC,%	18.72	0.00	0.00	0.00	0.00
OXYGEN CONC,%	31.26	0.00	0.00	0.00	0.00
NITRGN CONC,%	50.02	0.00	0.00	0.00	0.00
IN FLOW,MG MOL/MIN	25.60	0.00	0.00	0.00	0.00
W/F,G/(MG MOL/MIN)	0.50	0.00	0.00	0.00	0.00
OXYGEN:BUTANE	1.67	0.00	0.00	0.00	0.00
NITROGEN:OXYGEN	1.60	0.00	0.00	0.00	0.00

OUTLET CONCENTRATIONS

ETHYLENE,%	1.32	0.00	0.00	0.00	0.00
PROPELENE,%	0.93	0.00	0.00	0.00	0.00
N-BUTANE,%	12.28	0.00	0.00	0.00	0.00
N-BUTENE,%	0.31	0.00	0.00	0.00	0.00
TRANCE-2-BUTENE,%	0.31	0.00	0.00	0.00	0.00
CIS-2-BUTENE,%	0.31	0.00	0.00	0.00	0.00
1,3-BUTADIENE,%	0.98	0.00	0.00	0.00	0.00
METHANE,%	0.92	0.00	0.00	0.00	0.00
CARBON DIOXIDE,%	15.38	0.00	0.00	0.00	0.00
OXYGEN,%	6.99	0.00	0.00	0.00	0.00
CARBON MONOXIDE,%	4.69	0.00	0.00	0.00	0.00
NITROGEN,%	55.58	0.00	0.00	0.00	0.00
OUT FLOW,MG MOL/MIN	23.04	0.00	0.00	0.00	0-00

CONVERSION,YIELD,SELECTIVITY

CONVERSION,%	40.98	0.00	0.00	0.00	0.00
YIELD BD,%	4.69	0.00	0.00	0.00	0.00
YIELD BUTE(S)+BD,%	9.23	0.00	0.00	0.00	0.00
SELECT BD,%	11.45	0.00	0.00	0.00	0.00
SELECT BUTE(S)+BD,%	22.54	0.00	0.00	0.00	0.00